Tuğba İPEK

M.S. Thesis In Chemistry

June 2011

NOVEL PORPHYRAZINES BEARING EIGHT (2-ANTHRAQUINONYLMETHYLTHIO) GROUPS

by

Tuğba İPEK

June 2011

NOVEL PORPHYRAZINES BEARING EIGHT (2-ANTHRAQUINONYLMETHYLTHIO) GROUPS

by

Tuğba İPEK

June 2011

NOVEL PORPHYRAZINES BEARING EIGHT (2-ANTHRAQUINONYLMETHYLTHIO) GROUPS

by

Tuğba İPEK

A thesis submitted to

the Graduate Institute of Sciences and Engineering

of

Fatih University

in partial fulfillment of the requirements for the degree of

Master of Science

in

Chemistry

June 2011
Istanbul, Turkey

APPROVAL PAGE

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

_____
Prof. Dr. Cevdet NERGİZ
Head of Department

This is to certify that I have read this thesis and that in my opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

_____
Assoc. Prof. Ergün GONCA
Supervisor

Examining Committee Members

Assoc. Prof. Ergün GONCA _____

Assist. Prof. Ali Ekrem MÜFTÜOĞLU _____

Assoc. Prof. Bayram ÜNAL _____

It is approved that this thesis has been written in compliance with the formatting rules laid down by the Graduate Institute of Sciences and Engineering.

_____
Assoc. Prof. Nurullah ARSLAN
Director

June 2011

NOVEL PORPHYRAZINES BEARING EIGHT (2-ANTHRAQUINONYLMETHYLTHIO) GROUPS

By Tuğba İPEK

M. Sc. Thesis in Chemistry
June 2011

Supervisor: Assoc. Prof. Ergün GONCA

ABSTRACT

Porphyrins, phthalocyanines, tetrabenzoporphyrins and porphyrazines, which can be denoted as tetrapyrrole derivatives, receive extensive attention because of both theoretical studies and applications in advanced materials science. Among this group, porphyrins are important not only from biological aspect but also for coordination chemistry, catalysis and material science. Phthalocyanines that are completely synthetic materials are used in electro photography, optic data collection, gas sensor, liquid crystal, laser technology and the photodynamic therapy of tumors as well as their classical fields as pigments and dyes. Peripherally functionalized porphyrazines have the potential to exhibit novel optical, magnetic and electronic properties; also maintain some additional features superior to the values met in related materials. The transition metal ion in the inner core offers new ways to induce, modify and control molecular properties.

In this study, novel porphyrazines bearing eight (2-anthraquinonylmethylthio) substituents appending to the peripheral positions were synthesized. By cyclotetramerization of 2,3-bis(2-anthraquinonylmethylthio) maleonitrile in the presence of magnesium butanolate, magnesium porphyrazinate carrying eight (2-anthraquinonylmethylthio) functional groups on the peripheral positions has been synthesized. The metal-free derivative was obtained by its treatment with trifluoroacetic acid and further reaction of this product with copper(II) acetate, zinc(II) acetate and cobalt(II) acetate led to the metal porphyrazinates [M^{2+} = Cu^{2+}, Zn^{2+}, Co^{2+}].

These new compounds have been characterized by elemental analysis, together with FT- IR, ^{1}H NMR, ^{13}C NMR, UV-Vis and mass spectral data.

Keywords: 2-(chloromethyl)anthraquinone; porphyrazine; maleonitrile; copper; zinc.

(2-ANTRAKİNONİLMETİLTİYO) GRUBU İÇEREN YENİ PORFİRAZİNLER

Tuğba İPEK

Yüksek Lisans Tezi-Kimya Bölümü
Haziran 2011

Tez Yöneticisi: Doç. Dr. Ergün GONCA

ÖZ

Tetrapirol türevleri olarak gruplandırabileceğimiz porfirinler, ftalosiyaninler, tetrabenzoporfirinler ve porfirazinler son yıllarda hem temel bilim, hem de uygulamalı çalışmalar için üzerinde önemle durulan konulardan birini oluşturmaktadır. Bu gruptan porfirinler sadece biyoloji açısından önem taşımakla kalmayıp zengin koordinasyon kimyası, kataliz ve malzeme biliminde de önemli bir yere sahiptir. Tamamen sentetik ürünler olan ftalosiyaninlerin boyar madde ve pigment olarak değerlendirilmesi yanında elektrofotografi, optik veri toplanması, gaz sensör, sıvı kristal, lazer teknolojisi ve tümörlerin fotodinamik terapisinde kullanılmaktadır.

Periferal konumlarında fonksiyonel gruplar taşıyan porfirazinler yeni optik, manyetik ve elektronik özellikleri sergileyecek potansiyele sahiptir; aynı zamanda porfirazinlerin türevlendirilmesindeki bazı kolaylıklar, söz konusu maddelere olan ilginin artışını teyit etmiştir. İç kürede yer alan geçiş metal iyonu, moleküler özellikleri kontrol ve modifiye etme imkânlarını ortaya çıkarır.

Bu çalışmada periferal konumdaki sekiz adet (2-antrakinonilmetiltiyo) sübstitüentleri içeren porfirazinler sentezlendi. Magnezyum butanolat içerisinde 2,3-bis(2-antrakinonilmetiltiyo)maleonitril, siklotetramerizasyon yöntemiyle reaksiyon sonucunda magnezyum porfirazin sentezlendi. Trifloroasetik asit gibi kuvvetli bir asitle muamele edilerek metalsiz türevine geçildi ve bu ürünün bakır(II) asetat, çinko(II) asetat ve kobalt(II) asetat ile reaksiyona sokulmasıyla metalli porfirazinler elde edildi [M(II) = Cu(II), Zn(II), Co(II)].

Bu ürünlerin karakterizasyonu ^{1}H NMR, ^{13}C NMR, FT-IR, UV-Görünür bölge, kütle ve elementel analiz gibi çeşitli spektral verilerle gerçekleştirildi.

Anahtar Kelimeler: 2-(klorometil)antrakinon; porfirazin; maleonitril; bakır; çinko.

ACKNOWLEDGEMENTS

I am greatly indebted to my supervisor, Assoc. Prof. Ergün GONCA for informed guidance and advice extended to me throughout my work in this thesis.

All my colleagues at laboratory including Miss Didar, Zerrin, Melike are remembered for their kindness and co-operation at work.

Finally, I am grateful to my family who always directed to me towards studies. I would like to thank my fiance Cevat ERACAR for his love, support and patience during my study.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

M	Metal
CCC	Comprehensive Coordination Chemistry
H_2AP	Azaporphyrine
H_2DAP	Trans-diazaporphyrine
H_2MATBP	Monoazatetrabenzoporphyrine
H_2NTBP	Tribenzo (1-phenyl-2-3-naphthalo) porphyrine
H_2OED	Octaethylporphyrine
H_2OEP	2,3,7,8,12,13,17,18-octaethylporphyrin
H_2MAP	Monoazaporphyrine
H_2TATBP	Triazatetrabenzoporphyrine
H_2TBP	Tetrabenzoporphyrine
H_2TPP	Meso-tetraphenylporphyrine
H_2TPrP	Meso-tetra (n-propyl) porphyrine
HMDS	Hexamethyldisilazane
AP	Metalloazaporphyrine
HPLC	High-performance liquid chromatography
Pc	Phthalocyanine
PH_2	Porphine molecule
MPA	Metalloporphyrazine
PDT	Photo Dynamic Therapy
OL	Optical Limiting
MP	Metalloporphyrine
MTAP	Metallotetraazaporphyrine
FAB	Fast Atom Bombardment
EAS	Electron Absorption Spectrum
MO	Molecular Orbital
DCM	Dichloromethane
DMF	N,N-dimethylformamide
DCE	Dichloroethane

DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DBN	1,5-diazabicyclo[4.3.0]non-5-ene
DMAE	2-(N,N-dimethylamino)ethanol
NMR	Nuclear Magnetic Resonance
IR	Infrared
UV / VIS	Ultraviolet / Visible Spectrum
Å	Angstrom
Pyr	Pyrrole
LCAO	Linear Combination of Atomic Orbital
LUMO	Lowest Unoccupied Molecular Orbital
HOMO	Highest Occupied Molecular Orbital
L	Ligand
$M(P)L_4$	Metal monotetrapyrroles
$M(P)_2$	Bistetrapyrroles
$M_2(P)_3$	Tristetrapyrroles

CHAPTER 1

INTRODUCTION

Tetrapyrrole macrocycles such as porphyrins, tetraazaporphyrins, phthalocyanines and tetrabenzoporphyrins, modified by the attachment of peripheral substituents, receive extensive attention because of both theoretical studies and applications in advanced materials science (McCleverty and Meyer, 2004). Among this group, porphyrins are important not only from biological aspect but also for coordination chemistry, catalysis and material science. Peripherally-functionalized porphyrazines have the potential to exhibit novel optical, magnetic and electronic properties. The transition metal ion in the inner core offers new ways to induce, modify and to control molecular properties. Metalloporphyrazines have been also proven to exhibit optical limiting effects comparable with phthalocyanine and naphthalocyanine derivatives (Vagin, Barthel et al., 2003).

A 16 - membered electron rich conjugated planar macrocyclic core is common in all these structures. When this main core is composed of four pyrrol units bound to one another through methine (-CH=) bridges, it is called porphyrine (Figure 1.1.a). Four-benzo condensation on each of the pyrrol groups result with tetrabenzoporphyrine (Figure 1.1.b). Changing methine bridges with aza functions (=N-) in porphyrines result with porphyrazines (or tetraazaporphyrines) (Figure 1.1.c). The benzo-condensed porphyrazines are the well-known phthalocyanines (Figure 1.1.d).

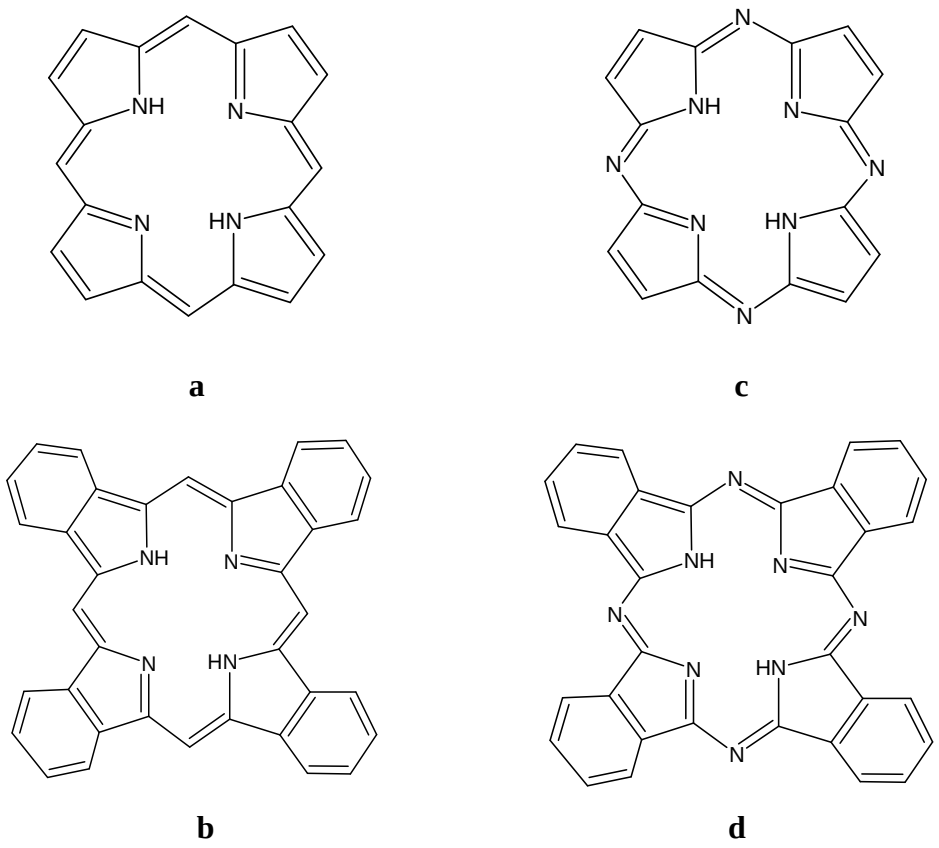


Figure 1.1 (**a**) Porphyrin, (**b**) Tetrabenzoporphyrin, (**c**) Porphyrazine, (**d**) Phthalocyanine.

All porphyrins, porphyrazine-type macrocycles share a common substructure which consists of four pyrrolic subunits. Like porphyrins, porphyrazines also contain a 22-π electron system, and this feature gains porphyrazines wide range of extraordinary properties such as the ability to absorb visible light, to mediate the conversion of absorbed light to other forms of chemical and physical energy, and to enhance thermodynamic and kinetic stability. These conjugated systems assume many resonance forms and can accept substituents at a number of positions (Mbatha, 2006).

Phthalocyanines that are completely synthetic materials are used in electrophotography, optic data collection, gas sensor, liquid crystal, laser technology and the photodynamic therapy of tumors as well as their classical fields as pigments and dyes. Tuning of the properties of phthalocyanines has been generally achieved through changes in the nature and bonding pattern of the substituents (McKeown, 1999).

Porphyrazines and related molecules have also been a theme of considerable theoretical interest due to their high symmetry, planar molecular arrangements, and

electronic delocalization. A large number of theoretical works have been devoted to the understanding of the atomic scale structure of these molecules, their building blocks and the mechanisms of charge transport and optical properties. Molecular design of porphyrazines for various Q-band splitting modes has attracted considerable experimental interest, where the ring symmetry modification has been introduced as a new methodology.

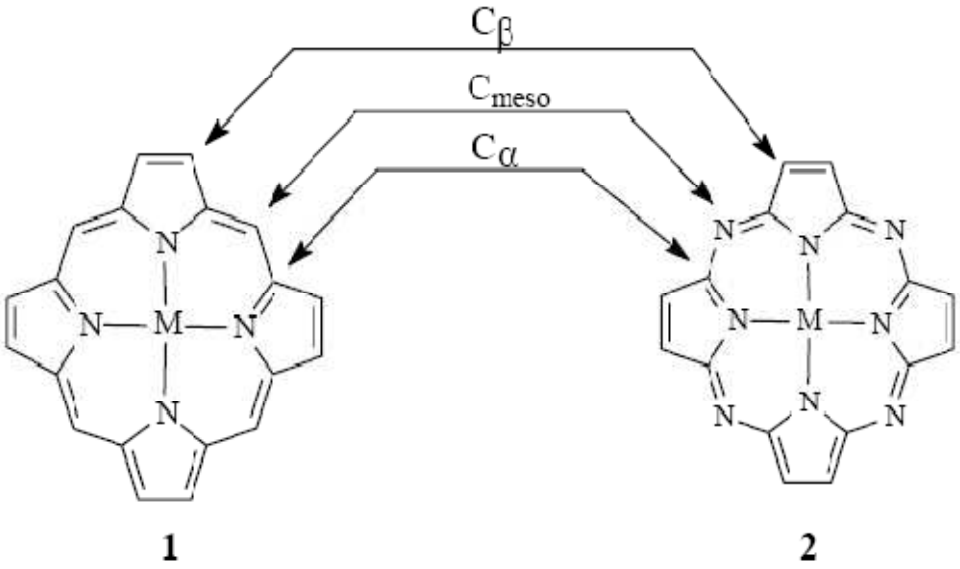


Figure 1.2 Tetrapyrrole-macrocycles (M=Metal or H_2), Porphyrin (**1**), Porphyrazine (**2**).

One of the most important properties of tetrapyrrol ligands is their ability to coordinate to metal ions, yielding stable inter complex salts. Stable complexes of porphyrins, porphyrazines (Fig. 1.1, Fig. 1.2) and phthalocyanines result from formation of four equivalent σ bonds (N → M) that is filling of vacant s, p_x, p_y and (n - 1) d_{x2-y2} or n d_{x2-y2} orbitals of the cation with σ electrons of the central nitrogen atoms which are called as coordinating N atoms. The chemical versatility of the porphyrazine macrocycle offers the opportunity of varying the electronic structure through ligand and metal modifications; this includes substitution, elaboration, and truncation of the macrocycle. Substitutions in a very controlled manner with certain electron-withdrawing or electron-donating groups to the macrocycle were found to change the electronic properties. The resulting σ bonds are strong that in the case of metals Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} that in solid complexes practically no replacement of the metal ions takes place at H_2SO_4 concentrations ranging from 2 to 7 M. In the case of coordination of triply or quadruply

charged ions the formation of a complex involves, in addition to d, s, and p^2 orbitals, p_z and d_{z2} orbitals that participate in the attachment of the extra ligand along the z-axis perpendicular to the plane of the molecule.

The formation of σ bonds (N →M) in porphyrin and porphyrazine complexes leads to four electron pairs of the coordinating nitrogen atoms being excluded from the conjugation. The antibonding π orbitals (π*) of the macroring are filled with the heteroatomic n orbitals. The attendant decrease in the energy of these antibonding π orbitals favors conjugation of the heteroatomic n electrons which have not taken any part in the coordination to the metal. As a result the remaining n electrons acquire a π rather than a σ character and are not easily protonated with acids. In many cases where the metal ion has filled d orbitals of π symmetry (d_{xy}, d_{xz}, d_{yz}) it forms backward dative π bonds with the macrocyclic tetrapyrrol ligand. The metal serves as a donor of π electrons and the ligand as their acceptor. These bonds are opposite in direction to σ bonds, that is M → N, and are called backbonding. The d-π electrons of the metal fill the antibonding π orbitals of porphyrazine. The filling of antibonding π orbitals increases their energy, which prevents the n electrons of the meso-N atoms from entering into a π conjugation as well as enhancing their σ character and capacity for acid protonation.

In addition to electronic and charge effects of coordination complexes with cyclic π ligands such as porphyrins, phthalocyanines, porphyrazines and other macroheterocyclic compounds, may in some cases display steric effects of coordination. If coordination distorts the planar structure of a conjugated cyclic system, the conjugation of n electrons of the nitrogen atoms with the macroring π system weakens. As a result the basicity of the molecules increases. If coordination to a metal creates a more coplanar π system than the ligand, the opposite is true.

The porphyrazine is isoelectronic with the porphyrin, but because of its nitrogen atoms at the meso positions chemically much closer to the technologically important phthalocyanines. To investigate the electronic properties of the phthalocyanines it is, therefore, necessary to address the influence of those nitrogens on the electronic structure.

In the visible absorption spectra of porphyrins, the highly conjugated aromatic macrocycle shows an intense absorption in the region of about 400 nm which is referred to as the Soret Band (Fig. 1.3). Visible spectra of porphyrins also show four weaker bands, the Q bands, at longer wavelengths from about 450-700 nm giving rise to reddish purple color of porphyrins (Mbatha, 1999).

The effects of meso-tetraaza substitution on the UV-Visible absorption bands of porphyrins are to date well documented. Porphyrazine complexes exhibit for instance a significant red shift and an intensification of the lowest energy $\pi \rightarrow \pi^*$ Q band, and a more complicated Soret band region due to additional $\pi \rightarrow \pi^*$ transitions introduced by azamethine groups (Leznoff and Lever, 1990-1996 ; Weiss, Kobayashi et al., 1965).

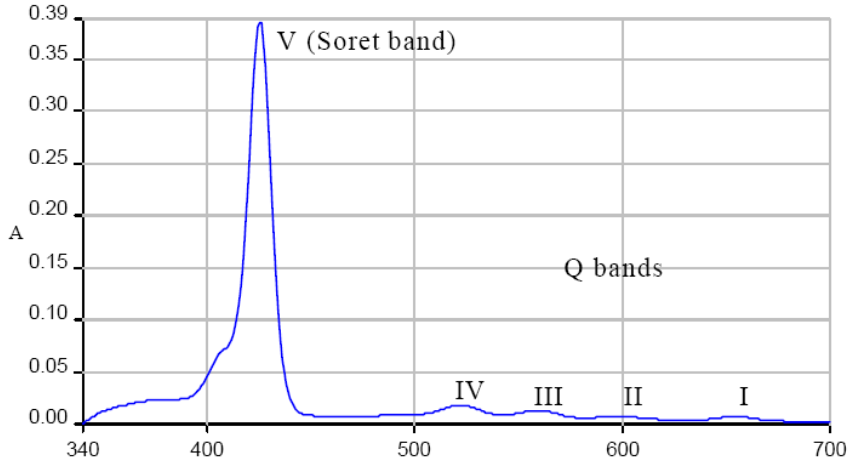


Figure 1.3 UV-Visible spectrum of a porphyrin.

The UV-visible spectra in porphyrazines are influenced by substituents and the presence or absence of a metal at the centre. Peripheral substitution influences the UV-visible spectra with *cis*- and *trans*- isomers showing different split in LUMOs. *Trans*-isomers show large splitting compared to *cis*-peripherally substituted porphyrazines. In non-metalated porphyrazines with reduced symmetry, reduction in symmetry removes degeneracy of e_g LUMO and gives a split Q-band (Fig. 1.4) (Stuzhin, Bauer et al., 1998). In cases where a lone pair of electrons in peripheral ligating atoms (N) becomes bonded to metal ions, the Q-band is split into two sharp bands (Fig. 1.5) because their interaction with the porphyrazine ring is suppressed (Stuzhin, Bauer et al., 1998).

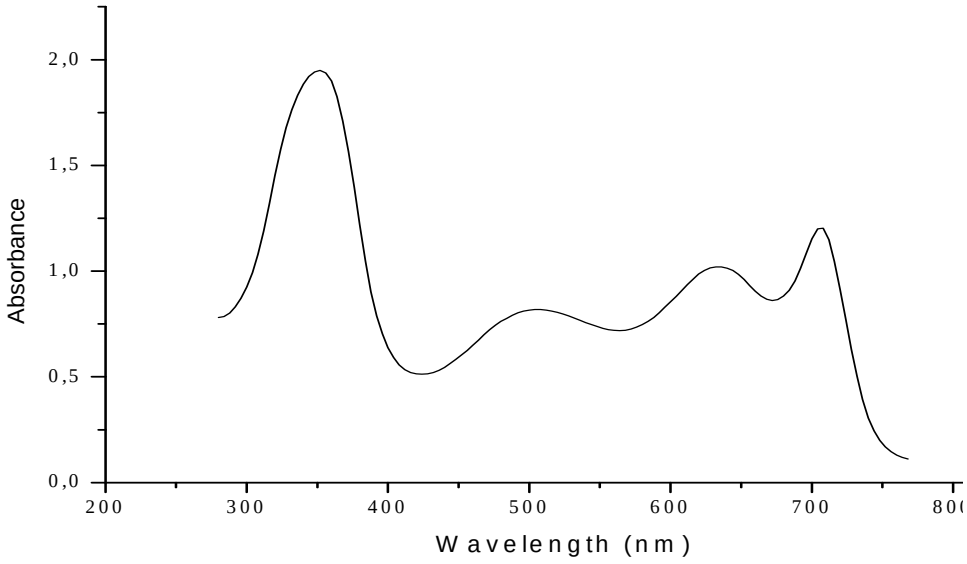


Figure 1.4 Electronic absorption spectrum of H_2Pz.

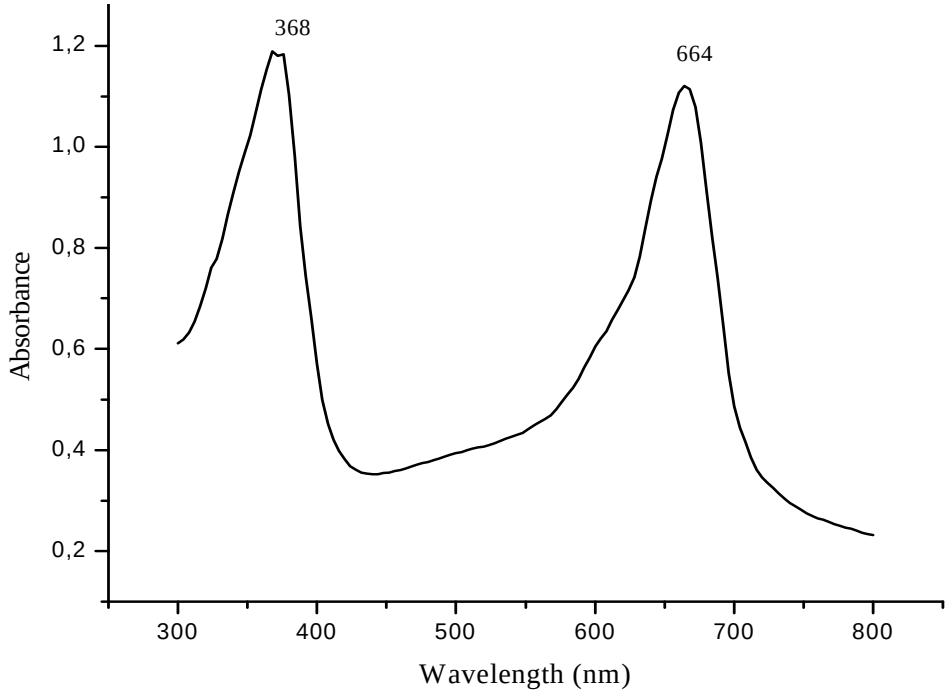


Figure 1.5 Electronic absorption spectrum of MgPz.

For nonmetalated (metal-free) porphyrazines (D_{2h} symmetry), the UV-visible spectra show two lower energy split Q-bands at 550-700 nm and a higher energy Soret (B) band at 300-400 nm, which are assigned to $a_u \rightarrow b_{2g}$ (Qx), $a_u \rightarrow b_{3g}$ (Qy) and $b_{1u} \rightarrow b_{2g}$ (Qx), $b_{1u} \rightarrow b_{3g}$ (B_y) transitions (Fig. 1.6). These transition bands are assigned to excitations from the two highest-occupied molecular orbitals (HOMO) (a_{1u} and a_{2u}) into

lowest unoccupied molecular orbitals (LUMO, e_g) (Stuzhin, Bauer et al., 1998 ; Sibert, Baumann et al., 1996). The lower energy peak which could be found at 400-500 nm is assigned to n-π* transitions from the lone-pair electrons in external meso-nitrogen atoms into a π* ring system.

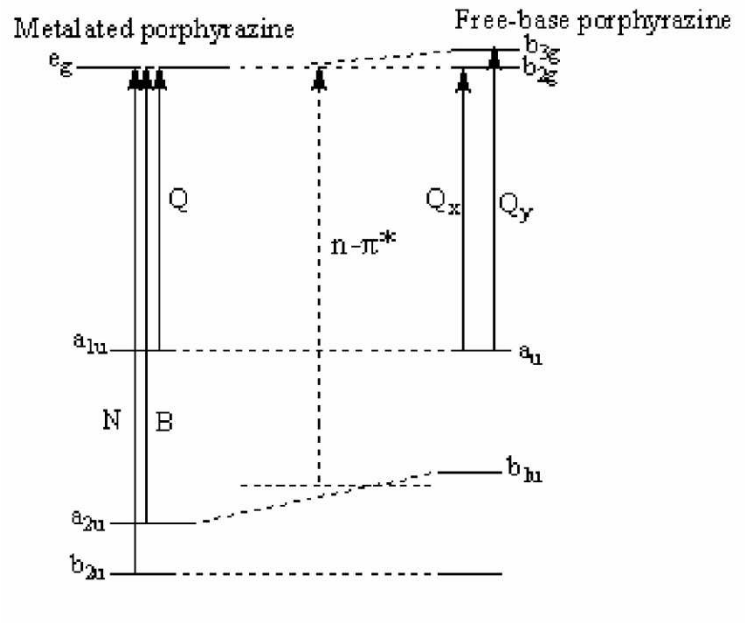


Figure 1.6 Electronic transitions in the visible and close UV regions of metalated and non-metalated porphyrazines.

Metalated porphyrazines exhibit two intense π → π* absorbances, a low energy Q band that is accompanied by a slight higher energy shoulder and a higher energy B band. For metalated porphyrazines, the symmetry of the chromophore is D_{4h} with the two LUMOs b_{2g} and b_{3g} giving rise to a two-fold degenerate e_g level resulting to an unsplit Q and B absorptions associated with transitions a_{1u} → e_g and a_{2u} → e_g (Cook and Jafari-Fini, 2000 ; Linßen and Hanack, 1994).

Porphyrazine, tetraazaporphyrine or, according to the IUPAC nomenclature, 2,7,12,17,21,22,23,24octaazapentacyclo[16,2,1,13,6,18,11,12,26]tetracosaundecaene), in its structure, occupies an intermediate position between other well studied tetrapyrrole macrocyclic systems, porphyrine and Pc. The conjugation system of the H_2Pzs molecule is multicontour, and its internal chromophore n-electrons (8 double bonds and 2 π-electrons of internal nitrogen atoms) (Kopranenkov and Luk'yanets, 1995).

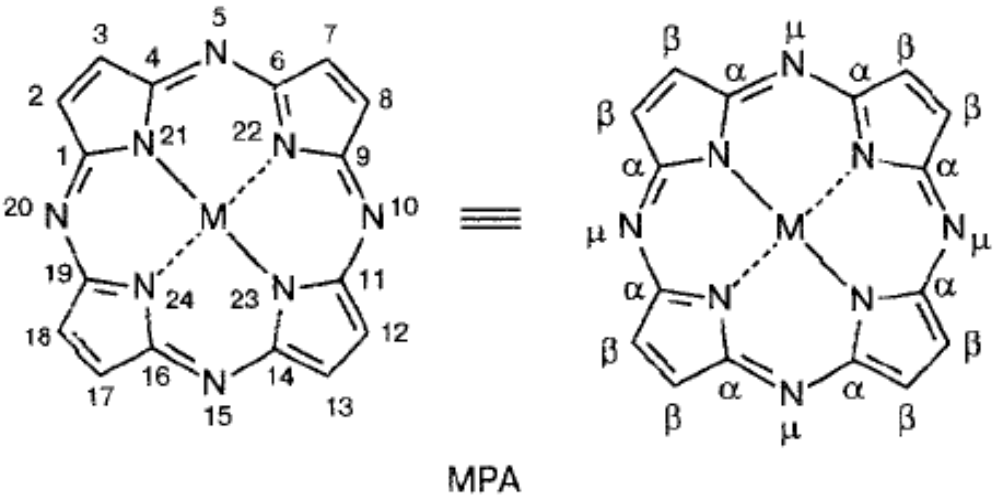


Figure 1.7 General structure of porphyrazine molecules.

The skeleton of common porphyrin ligands can be considered as almost planar since the deviations of the C and N atoms from the mean plane do not exceed 0.006 nm. The symmetry of the skeleton is in most cases D_{2h}. A D_{4h} skeletal symmetry was found for monoclinic H_2P and tetragonal H_2TPP. D_{2h} distortion of the porphyrin ligands is connected above all with the inequivalent of the five-membered rings composing the macrocycle. In two trans-located pyrrole type-rings (A) the bonds C_α-C_β are about 0.002-0.003 nm shorter, C_β-C_β bonds are about 0.002 nm longer and the inner angle formed by the nitrogen atom is 2.5-4^o larger compared with a pair of the neighboring pyrrolenine-type rings. At the same time the bond lengths between C_α atoms and the inner nitrogen atoms vary only slightly in these two ring types and are 0.002-0.003 nm shorter than the bonds of C_α atom with C_{meso} atom (Fig. 1.8). The symmetric alkyl or aryl substitution in the meso or β positions has little influence the changes in the bond lengths and values of the angles do not exceed 0.002 nm and 2^o. The dimensions of the central coordination cavity (measured as a distance between the intracyclic N atoms N_{pyr} and macrocycle center C_t) vary slightly in the range 0.204-0.206 nm (Table 1.1). One can expect that the direct substitution of the carbon atom in the conjugated π system of the porphyrin with a heteroatom, namely aza-substitution in the meso positions, should produce significantly greater changes in the geometry of the reaction center and that is the case in fact.

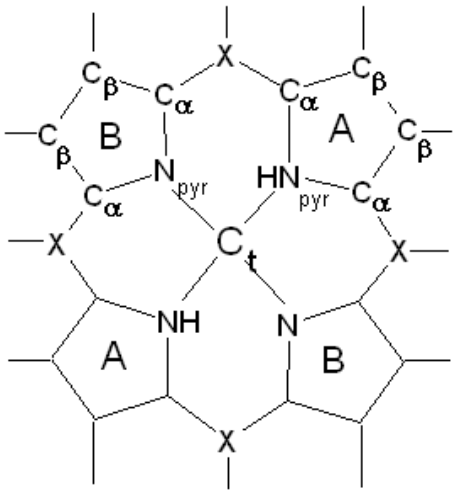


Figure 1.8 Pyrrole-type and Pyrrolenine-type Rings.

Table 1.1 Average geometrical parameters for the CN skeleton of porphyrin and azaporphyrin ligands.

Geometric parameter	H_2P[a]	H_2OEP[a]	H_2TPP[a]	H_2MATBP	H_2Pc	H_2Pc	H_2TAP
C_α-X (nm)	0.1376 0.1387	0.1390	0.1400	0.125 (N) 0.139 (C)	0.1335	0.132	0.133
C_α-N_{pyr} (nm)	0.1377 0.1380	0.1364 0.1367	0.1364 0.1374	0.145	0.1340	0.137	0.136
C_α-C_β (nm)	0.1452 0.1431	0.1462 0.1438	0.1455 0.1428	0.147	0.1490	0.147	0.144
C_β-C_β (nm)	0.1345 0.1365	0.1353 0.1373	0.1347 0.1355	0.152	0.1390	0.140	0.134
N_{pyr}- C_t (nm)	0.2051	0.2062	0.2060		0.1913		0.194
C_α-X-C_α (^{0})	126.9	127.7	125.6	111 (N) 143 (C)	115 119	122 125	122
C_α-N_{pyr}-C_α (^{0})	106.1 108.5	105.7 109.6	106.2 109.2	109	109	109	108
X-C_α-N_{pyr} (^{0})	125.1	125.0	126.2	132 (N) 123 (C)	131	127 130	128

CHAPTER 2

GENERAL INFORMATION ABOUT TETRAPYRROL DERIVATIVES

2.1 Phthalocyanine Complexes

Phthalocyanine (Pc), together with its derivatives, comprises one of the most studied classes of functional organic materials. It is a planar, aromatic macrocycle comprised of four iminoisoindole units that can play host to ions derived from over 70 elements. The coordination chemistry of the Pc ligand, which usually possesses a formal charge of 2^-, is a rich and extensive subject. Without the intervention of a metal ion, only the simple tetraiminoisoindoline ligand exists. In addition, subphthalocyanine (Fig. 2.2), composed of three iminoisoindoline subunits, and superphthalocyanine, composed of five iminoisoindoline units, are known, but only as complexes with B^{3+} and UO^{2+}, respectively. Other unusual metal complexes involving the Pc ligand are sandwich dimers and trimers, in which two Pc ligands share the same metal ion. There are also nonaromatic, stapled sandwich complexes, and bicyclic Pcs in which six iminoindole units ligate a single metal ion (Geyer, Plenzig et al., 1996 ; Capobianchi, Ercolani et al., 1993 ; Janczak and Kubiak, 1994).

The diverse and useful functionality of the Pc macrocycle originates from its 18-π-electron aromatic system, which is closely related to that of the naturally occurring porphyrin ring. The additional π-orbital conjugation afforded by the four benzo-moieties, and the orbital perturbation caused by the nitrogen atoms at the four meso-positions, have a profound effect on the molecular orbital structure of the porphyrin chromophore. This results in a bathochromic shift of the lowest-energy absorption band (the Q-band) in the visible region of the spectrum, and a strong enhancement of its intensity (typically $\lambda_{max} \sim 680$ nm, $\varepsilon \sim 2\times10^5$ cm^2 mol^{-1}). The basic spectroscopic properties of Pcs were covered in CCC (1987). Their strong color, coupled with renowned chemical and thermal stability, explains the ubiquitous use of

phthalocyanines as highly stable blue (or green) pigments and dyes, and this important commercial aspect has been reviewed and outlined in CCC (1987) (Price and Wilkinson, 1987).

In addition, phthalocyanines are exploited commercially for optical data storage, catalysis, and as photoconductors in xerography. They are also of interest as materials for nonlinear optics, liquid crystals, ordered thin films, photodynamic cancer therapy, molecular semiconductors, components of highly conducting charge-transfer salts and polymers, photovoltaic devices, electrochromic devices, fuel cells, and sensors. The synthesis of phthalocyanine and its substituted derivatives is often driven by the desire to exploit and improve performance in one of these technological arenas. Unlike Pc itself, many substituted derivatives are soluble in common organic solvents. There are a number of useful reviews dealing with the synthesis of Pcs (McKeown and Weinreb, 2003).

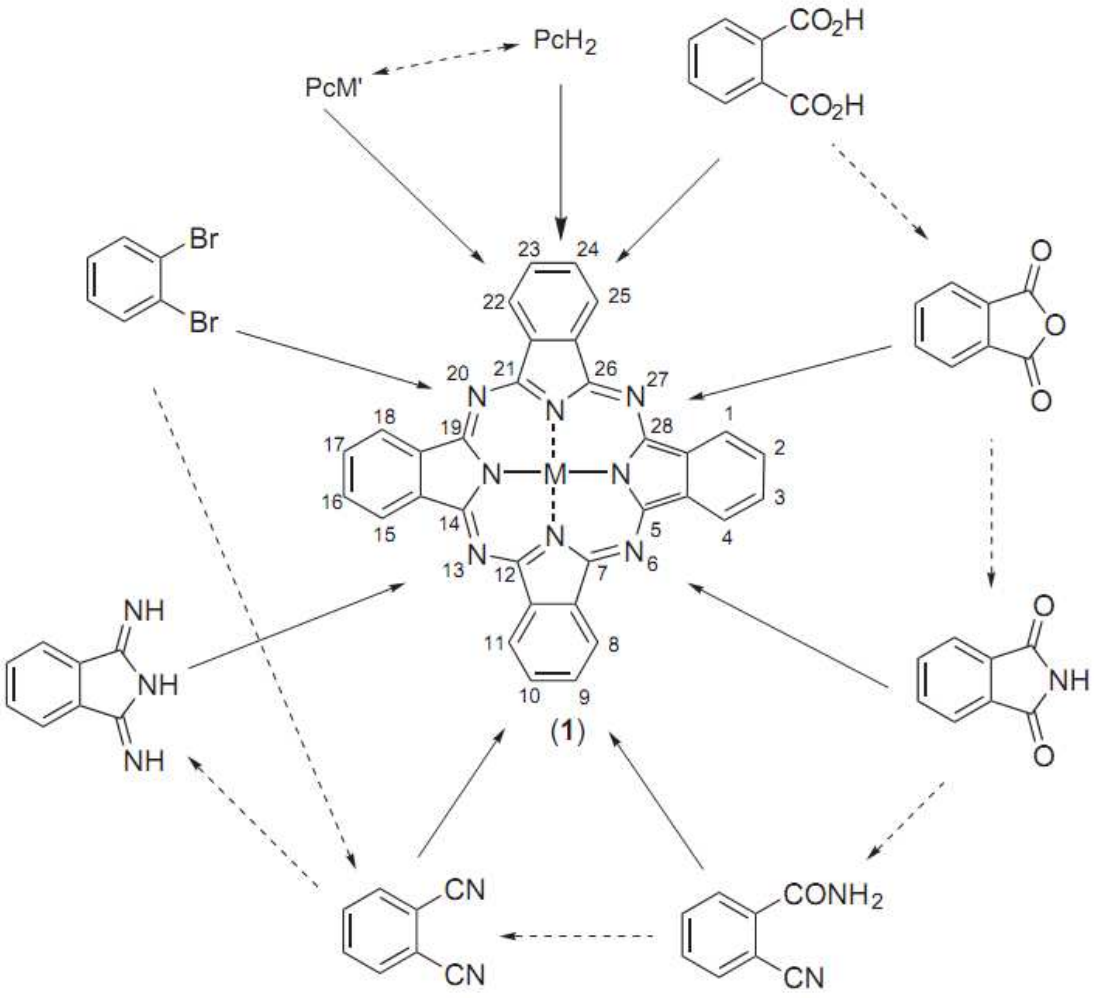


Figure 2.1 The synthetic connectivities between various precursors in Pc.

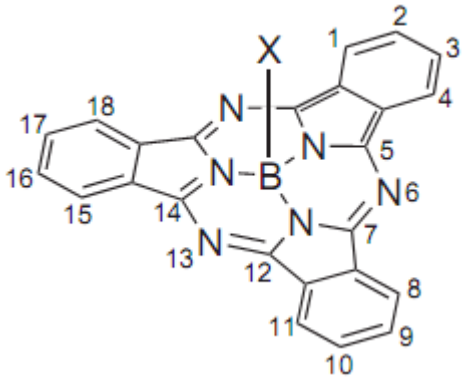


Figure 2.2 Subphthalocyanine.

2.1.1 General Synthetic Considerations

The most common synthetic method for the synthesis of metal-containing Pcs involves the cyclotetramerization of phthalic acid, phthalic anhydride, 2-cyanobenzamide, phthalimide, diiminoisoindoline, or phthalonitrile at elevated temperatures (>200 °C) in the presence of a metal or metal salt. These reactions can be carried out either in a suitable solvent or in the melt. It should be noted that the use of a metal halide in the melt often leads to a monohalogenated Pc. Except for phthalonitrile and diiminoisoindoline cyclotetramerizations, a nitrogen source is required,which is usually urea. In addition, 1,2-dibromobenzene can be used as a precursor to $PcCu^{2+}$ by the in situ preparation and cyclotetramerization of phthalonitrile by the action of copper(I) cyanide (the Rosenmund–von Braun reaction). Metal complexes can be prepared by the addition of a metal ion to the free ligand (**1**) (M = $2H^{+}$), or by transmetalation using labile complexes containing alkali-metal ions (e.g., Li_2 (**1**) or Na_2 (**1**)). The latter method exploits the solubility of alkali-metal Pcs in polar solvents (Barrett, Frye et al., 1938). The synthetic connectivities between these various precursors are shown in Figure 2.1. Most synthesis of the metal-free ligand (**1**) (M = $2H^{+}$) use either phthalonitrile or diiminoisoindoline as the starting material. Great care must be taken during its preparation to avoid unintentional incorporation of metal ions. The direct cyclotetramerization of phthalonitrile to give phthalocyanine requires a two-

electron reduction and the donation of two protons from a co-reactant or solvent. Reagents such as hydroquinone and 1,2,3,6-tetrahydropyridine are particularly effective, and a good yield of phthalocyanine can be achieved from the incorporation of these reducing agents into cyclotetramerizations carried out in the melt (~275 °C) (Thompson, Murata et al., 1993). Alternatively,cyclotetramerization can be achieved by heating phthalonitrile in a solution of lithium (or sodium) dissolved in a primary alcohol (e.g., pentanol) and washing out the labile alkali-metal ion from the resulting Pc with aqueous acid (this is known as the ‘‘Linstead method’’) (Barrett, Frye et al., 1938). A recent modification of the Linstead method involves leaving a solution of the phthalonitrile and alkoxide in alcohol (particularly, octan-1-ol) for prolonged periods at moderate (~60 °C) or even at room temperature. A related procedure to that of the Linstead reaction involves the use of a catalytic amount of a non-nucleophilic base, such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), to initiate cyclotetramerization in a protic solvent such as n-pentan-1-ol or 2-(N,N-dimethylamino)ethanol (DMAE). Diiminoisoindoline, an addition product of ammonia and phthalonitrile, can form Pc in good yield simply by heating in a protic solvent (Leznoff, D’Ascanio et al., 2000).

2.1.2 Substituted Phthalocyanine Ligands

The Pc ligand offers a total of sixteen sites—four on each benzo unit—for the attachment of substituents, and an astonishing number of substituted derivatives of (**1**) have been prepared since the start of the 1980s (McKeown and Weinreb, 2003). In most cases, a substituted phthalonitrile or the derived diiminoisoindoline is used as precursor. However, the commercially important chlorinated Pcs and the water-soluble tetrasulfonate Pcs derivatives are usually prepared from the metal-ion-induced cyclotetramerization of the appropriate phthalic acid derivative in a urea melt. The examples of substituted Pcs given in Table 2.1 are restricted to metal-free systems, although metal-containing derivatives were often reported, prepared either by a metal-ion-mediated cyclotetramerization or by insertion of a metal ion into the preformed ligand (Mikhalenko, Korobkova et al., 1970).

Tetrasubstituted derivatives substituted at four of the peripheral (2,3,9,10,16,17,23,24) or the nonperipheral (1,2,8,11,15,18,22,25) sites are usually

prepared as a statistical mixture of four isomers of C_{4h}, C_{2v}, C_s, and D_{2h} symmetry. The isomeric heterogeneity of Pcs derived from 4-substituted phthalonitriles is beneficial for attaining soluble derivatives. For example, (**1b**) is highly soluble in common organic solvents, but the four t-butyl substituents do not affect the spectroscopic or electrochemical properties of the ligand significantly. However, it is possible to prepare isomerically pure 1,8,15,22-tetrasubstituted Pcs (C_{4h} isomer) by exploiting steric and electronic factors that result in a regioselective cyclotetramerization of the 3-substituted phthalonitrile (e.g. (**1a**)). The mild conditions afforded by low-temperature cyclotetramerization reactions favour regiospecific formation. Even for nonregioselective reactions, it is often possible to isolate this isomer by chromatography (e.g. HPLC) or by recrystallization.

Soluble and isomerically pure derivatives, such as (**1c–1e**), can be obtained by the cyclotetramerization of 3,6- or 4,5-disubstituted phthalonitriles to give 1,4,8,11,15,18,22,25 and 2,3,9,10,16,17,23,24-octasubstituted Pcs, respectively. Octa-alkyl derivatives with long alkyl chains ($>C_5H_{11}$) form columnar liquid crystals.Nonperipheral substitution with alkyloxy side chains, e.g. (**1d**), results in a large red shift of the primary absorption band in the visible region of the spectrum from ~680 nm to ~780 nm. Similarly, Pcs with hexadeca alkyloxy or pyrazol-1-yl substituents (e.g. (**1g**)) also have Q-bands in the near-IR region of the spectrum. An active area of research since the mid-1980s has been the synthesis and study of Pcs with crown ether or aza-crown units fused to their peripheral sites (e.g. (**1f**)). These systems can be used for the assembly of multinuclear metal-ion complexes.

Table 2.1 Examples of substituted Pcs.

	Substituents	*Reagents and conditions*	*Yield*
(1a)	1,8,15,22-$(OCH_2$-*t*-Bu$)_4$	1. 3-neopentylphthalonitrile, Li, 1-octanol, 60 °C, 2 h; 100 °C, 12 h; 120 °C, 2 h; 2. H_2O	30
(1b)	2,9(10),16(17),23(24)-(*t*-Bu$)_4$	1. 4-*t*-butylphthalonitrile, Na, *i*-pentan-1-ol, reflux, 5 h; 2. MeOH, rt, 3 h	57
(1c)	1,4,8,11,15,18,22,15-(*n*-$C_7H_{15})_8$	1. 3,6-di-*n*-heptylphthalonitrile, Li, pentan-1-ol, reflux, 1 h; 2. AcOH, rt, 10 min	22
(1d)	1,4,8,11,15,18,22,15-(OEt$)_8$	1. 3,6-diethyloxyphthalonitrile, Li, pentan-1-ol, reflux, 0.25 h; 2. AcOH, rt, 0.5 h pentanol, 130 °C	20
(1e)	2,3,9,10,16,17,23,24-(*n*-$C_5H_{11})_8$	5,6-di-*n*-pentyldiiminoisoindoline, DMAE, reflux, 1 h	21
(1f)	2∩3,9∩10,16∩17,23∩24-$[O(CH_2CH_2O)_5]_4$-[a]	4′,5′-dicyanobenzo-18-crown-6, DMAE, reflux, 20 h	26
(1g)	1,2,3,4,8,9,10,11,14,16,17,18,22,23,24,15-(pyrazol-1-yl$)_{16}$	3,4,5,6-tetra(pyrazol-1-yl)phthalonitrile, hydroquinone, 180 °C	70
(1h)	1,4,8,11,15,18,22,15-octaaza-2,3,9,10,16,17,23,24-(*n*-$C_{12}H_{25})_8$	2,3-dicyano-5,6-di-*n*-dodecylpyrazine, DBU, EtOH, reflux, 20 h	14
(2)	X = Cl	Phthalonitrile, BCl_3,1-chloronaphthalene, 150–180 °C	40
(2a)	2,3,9,10,16,17-(S$C_6H_{13})_6$; X = Cl	4,5-dihexylsulfanylphthalonitrile; BCl_3, 1-chloronaphthalene, argon, 100 °C, 4 h	28
(3a)	2,3,7,8,12,13,17,18-(S$C_8H_{17})_8$	1. 1,2-dioctylsulfanylmaleonitrile; $Mg(OPr)_2$, PrOH, reflux; 2. TFA, CH_2Cl_3, reflux, 0.5 h	43
(4a)	3,4,12,13,21,22,26,27-(*n*-decyl$)_8$	1. 6,7-di-*n*-decylnaphthalonitrile, 1 equiv. LiOPe, pentanol, reflux, 6 h; 2. AcOH	26

[a] The symbols ∩ indicate that each of the four crown ether substituents are fused across the peripheral sites.

2.1.3 Nonuniformly Substituted Phthalocyanines

Phthalocyanines that possess two types of substituents on different benzo units are termed nonuniformly substituted, or unsymmetrical, phthalocyanines. There are three possible substitution patterns: where one of the benzo units is substituted differently from the other three (AAAB); where adjacent benzo units possess the same substituents (‘‘adjacent,’’ or AABB); and where opposite benzo units possess the same substituents (‘‘opposite,’’ or ABAB). Mixedcyclotetramerizations between two different Pc precursors (e.g., A and B) can give up to six distinct products (AAAB, AABB, ABAB,

and ABBB, and the two symmetrical phthalocyanines (AAAA and BBBB), derived from four molecules of the same precursor. The amount of each phthalocyanine obtained is related to the molar ratio of the two precursors and to their relative reactivity. For a reaction of an equimolar amount of two precursors of equal reactivity, a statistical analysis estimates that, of the total phthalocyanine yield, a product mixture of 6.25% AAAA (and BBBB), 25% AAAB (and ABBB), 12.5% ABAB, and 25% AABB will be produced. Clearly, careful separation of this complex product mixture is required if pure materials are to be isolated. Chromatographic separation is made far easier if the two types of substituents are of differing polarity (e.g. alkyl and polyethyleneoxy side chains). It is possible to optimize the formation of the AAAB product by using an excess of precursor A relative to precursor B. This ensures that the only two phthalocyanine products formed in significant quantities are the symmetrical AAAA derivative and the required AAAB phthalocyanine (Clarkson, Cook et al., 1996). An alternative route to AAAB-type unsymmetrical Pcs is provided by the ring-expansion reaction of a subphthalocyanine (Fig. 2.2) (itself prepared by the cyclotrimerization of a phthalonitrile about a borane: Table 2.1) with a diiminoisoindoline. Although this method appears to offer greater selectivity over the mixed cyclotetramerization approach, there are a number of drawbacks. These include possible halogenation of the resulting phthalocyanine; the need for removal of excess subphthalocyanine or isoindolinediimine by chromatography; and the scrambling of components, leading to unwanted phthalocyanine products, due to the partial fragmentation of the subphthalocyanine (de la Torre, Claessens et al., 2000). Despite these problems, useful yields can be achieved for particular combinations of substituents, especially for reaction systems in which the subphthalocyanine possesses electron-withdrawing groups and the isoindolinediimine has an electron-donating substituent. Polymer-supported methodology, in which the B precursor is attached to polymer substrate via an acid-labile linking group during the mixed cyclotetramerization, has also been shown to provide a selective route to AAAB-type Pcs (Kudrevich, Brasseur et al., 1997).

The dimeric intermediate formed from the initial stages of phthalonitrile cyclotetramerization can be used to form AABB-type Pcs (‘‘adjacent’’ isomer) selectively. The required ‘‘dimer’’ has been prepared from the reaction of phthalonitrile, 4-nitrophthalonitrile, or 4,5-bis(30,30-dimethyl-10-butynyl)phthalonitrile with lithium

methoxide in refluxing methanol. These intermediates react with different phthalonitriles under conventional cyclotetramerization conditions to give reasonable yields of AABB Pc, although significant quantities of the other unsymmetrical Pcs are formed. Similarly, the mixed cyclotetramerization of an appropriate bis(phthalonitrile), or its isoindolinediimine derivative, with an excess of another phthalonitrile (or isoindolinediimine) can provide AABB-type phthalocyanines which possess a single bridging unit between two adjacent benzo units of the macrocycle (Miwa and Kobayashi, 1999).

A useful route to ABAB-type (‘‘opposite’’ isomer) uses the two-stage cross-condensation of 1,3,3-trichloroisoindoline and isoindolinediimine. The success of this reaction relies on the inability of 1,3,3-trichloroisoindoline to undergo self-condensation, and the greater reactivity of isoindolinediimine towards 1,3,3-trichloroisoindoline, rather than self-cyclotetramerization. Although some AAAB-type phthalocyanine has been isolated from such a cross-cyclotetramerization reaction, the desired ABAB-type phthalocyanine is usually formed with high selectivity.The use of phthalonitrile precursors with bulky substituents in the 3,6-positions can help to improve the relative yield of ABAB-type Pcs in conventional mixed cyclotetramerization reactions (Stihler, Hauschel et al., 1997).

2.1.4 Azaphthalocyanines

There are many examples of phthalocyanine derivatives, given the general designation azaphthalocyanines, in which one (or two) of the carbons in each benzo unit is replaced by a nitrogen. The synthesis and properties of such macrocycles has been the subject of a detailed review. The physical properties of azaphthalocyanines differ from those of phthalocyanines. For example, they form hydrates readily, which complicates purification; and they are protonated by, and soluble in, dilute acids. In addition, the Q-band in the UV/visible absorption spectrum is blue shifted relative to that of phthalocyanine. Importantly, the aza moiety can be quaternerized to give water-soluble or amphiphilic derivatives (Kudrevich and van Lier, 1996). Thus, the cyclotetramerization of symmetrical 2,3-dicyanopyrazines provides a route to isomerically pure 1,4,8,11,15,18,22,25-octaazaphthalocyanines. The ease of synthesis of substituted 2,3-dicyanopyrazines has allowed the preparation of 1,4,8,11,15,18,22,25-

octaazaphthalocyanines with a variety of substituents attached to each of the remaining 2,3,9,10,16,17,23,24 positions (e.g. (**1h**)). These include alkyl and alkyloxy side-chains (Mørkved, Kjosen et al., 1999).

2.1.5 Extended Phthalocyanines

Phthalocyanines that contain four benzo units fused to the ring are termed naphthalocyanines. If the benzo units are fused to the 1,2,8,9(10,11),15,16(17,18),22,23(24,25)-positions, the parent compound is termed 1,2-naphthalocyanine; alternatively, if fused to the 2,3,8,9,16,17,23,24-positions, it is called 2,3-naphthalocyanine (Fig. 2.3). The linear benzoannulation of 2,3-napthalocyanines results in a bathochromic shift of the Q-band in the absorption spectrum of ~100 nm as compared to phthalocyanine (Kobayashi, Nakajima et al., 1993). In addition, their enhanced ability to generate singlet oxygen makes them candidates for photodynamic therapy. Most synthetic routes to 2,3-naphthalocyanines involve either a 2,3-dicyanonaphthalene (2,3-naphthalonitrile)

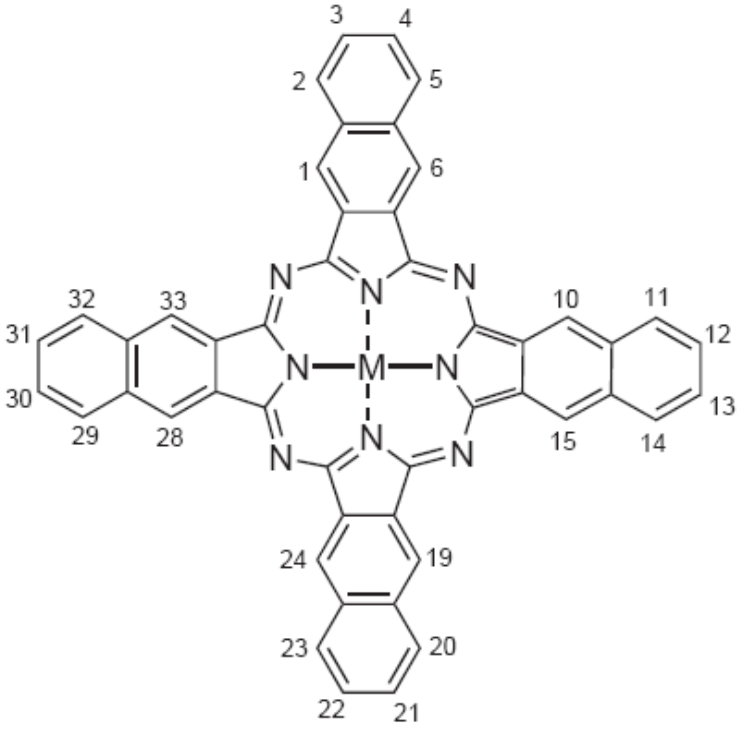


Figure 2.3 2,3-naphthalocyanine.

or benzoisoindolinediimine derivative as precursor, and the ‘‘normal’’ cyclotetramerization reaction conditions work well (Table 2.1). However, purification

and characterization can be problematic, as 2,3- naphthalocyanines show an even greater tendency than phthalocyanines to aggregate in solution. For some derivatives, especially those containing Zn^{2+} ions in the central cavity, care must be taken during purification to avoid exposure to strong light, as these compounds are prone to photodegradation via singlet oxygen generation. Other extended Pcs can be derived from the cyclotetramerization of 9,10-dicyanophenanthrene (phenanthrocyanine), from 2,3-dicyanotriphenylene (2,3-triphenylenocyanine), and from 2,3-dicyanoanthracene (2,3-anthracenocyanines) (Hanack and Renz, 1990).

2.2 Porphyrazine Complexes

Porphyrazines and their structural analogs belong to a broad class of macroheterocyclic tetrapyrrole systems that are constitutionally tetraaza analogues of porphyrins. These porphyrins are of considerable interest because their representatives are components of the most important natural compounds (hemoglobin, myoglobin, cytochromes, chlorophylls, and others) and are involved in such vital processes including photosynthesis, cell respiration, and electron transport.

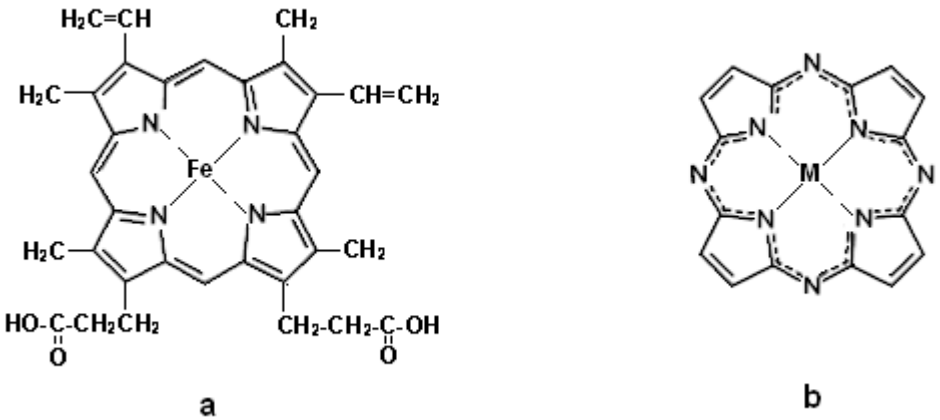


Figure 2.4 Hemoglobin (**a**) as a natural porphyrin and the simplest porphyrazine (**b**).

Recently, heteroatomic substitutions directly fusing to the macrocyclic periphery have brought an increasing attention to the porphyrazine studies (Michel, Baum et al., 2001 ; Stuzhin and Ercolani, 2003 ; Rodriguez-Morgade and Stuzhin, 2004 ; Montalban, Baum et al., 2003). Relative ease of their synthetic preparation, and also the strong correlation between the nature of the substituent and the electronic and optical

properties of the macrocyclic ring system play roles on this recent interest. Comparing to the phthalocyanine analogues, direct fusion of heteroatomic substituents onto the porphyrazine β-positions results in an evident effect; on the other hand, there is no such accessible analogous derivatives for the porphyrins.

In comparison to the phthalocyanine counterparts, the porphyrazines also often display a vastly increased solubility in organic solvents. Thus, they maintain a unique position among the tetrapyrrolic macrocycles, and their straightforward synthesis coupled with their tuneable electronic and optical properties, renders them exciting candidates for a whole range of applications (Fuchter, Zhong et al., 2008).

Porphyrazines are considerably less studied than phthalocyanines. There have been several positive properties of porphyrazines, specifically those closest to synthetic analogs of phthalocyanines and their high stability against oxidation favoring their use in wide practical application as dyes and pigments. Recently, porphyrazines have found several applications in new fields such as bleachable dyes in laser technique, discotic liquid crystals, components of electrochromic and electrophotographic materials, gas sensors, radiation protectors, catalysts of various processes (in particular, electrochemical), antimicrobial drugs, in luminescent diagnostics and photodynamic therapy of cancer tumors (Moser and Thomas, 1983 ; Leznoff and Lever, 1989).

2.2.1 Applications of Porphyrazines

2.2.1.1 Porphyrazines as Catalysts

The enhanced stability of porphyrazine derivatives toward the action of oxidants compared to phthalocyanines and porphyrins brings them into the class of very promising catalysts of various oxidation processes. The studies in this direction have emerged for the creation of efficient and stable catalysts within this class of compounds. For example, the introduction of 10^{-4}-10^{-5} mol L^{-1} of Co^{2+} porphyrazine increases the reaction rate and the selectivity of styrene transformation in the liquid-phase oxidation of styrene by molecular oxygen in chlorobenzene at 120 °C (Svetkina, Filippova et al., 1984). The epoxidation is realized by activated oxygen due to the formation of its complex with the catalyst. Mn^{3+} porphyrazine complexes are also efficient catalysts of olefin epoxidation by peracetic acid under mild conditions (Banfi, Montanari et al.,

1995). Further search for efficient catalysts of hydroxylation of saturated hydrocarbons like cytochrome P-450 was accomplished by porphyrazines.

The Porphyazines have found to be most suitable than the porphyrins and phthalocanines (Kaliya and Luk'yanets, 1986). For example, the oxidation of cyclohexane by cumene hydroperoxide in presence of Co^{2+} and Fe^{2+} porphyrazines complexes gives a mixture of cyclohexanol and cyclohexanone with an overall yield of 60%. In case of tetracyanotetrakis(o-trifluoromethylphenyl)-Co(II) porphyrazine, the yield of cyclohexanol and cyclohexanone was 74 % and the catalyst is completely retained, while Co^{2+} phthalocaynine completely decomposed under analogous conditions. Zn-poprhyrazine is an efficient sensitizer for the photochemical oxidation of 1,5-dihydroxynaphthalene by air oxygen to form 5-hydroxy-l,4-naphthoquinone (juglone), the known preservative for food industry (Kopranenkov and Luk'yanets, 1995).

One area of interest for the application of the metalloporphyrazines lies in their ability to act as catalysts for organic transformations. Perhaps in part, because of their similarity to the naturally occurring porphyrinic oxygenase enzymes, many reports have focused on their use as oxidation catalysts. For example, Deng and coworkers have explored the use of iron(II) thioporphyrazines in the oxidative degradation of organic pollutants, which mimic the structure of iron-containing cytochrome P450 enzymes (Sun, Sun et al., 2007 ; Deng, Huang et al., 2004). In these studies, catalytic thioporphyrazines, in combination with hydrogen peroxide, were examined in the oxidative degradation of Rhodamine B. Related studies by this group has examined the immobilization of such catalysts on anion-exchange resins (Lui, Han et al., 2004 ; Lei, Sun et al., 2005). Other studies of metal-catalyzed transformations using porphyrazine ligands include the catalytic antioxidant behaviour of manganese(II)/(III) Porphyrazines, and the use of oxygen-appended macrocycles as epoxidation catalysts (Spasojevic and Batinic-Haberle, 2001 ; Hachiya, Cook et al., 2000).

2.2.1.2 Biomedical Agents

Phthalocyanine derivatives can be utilized as sensitizers in photodynamic therapy of cancer (PDT). Sensitizers for PDT require high photostability, high selectivity to tumors, no dark cytotoxity, strong absorption in the region between 600 and 800 nm

where penetration of tissue is good, a long triplet lifetime, and satisfactory photosensitization of singlet oxygen. Phthalocyanine derivatives are known to satisfy the aforementioned conditions (Hirohashi, Sakamoto et al., 2004 ; Okura, 2000 ; Tabata, Fukushima et al., 2000). Nyokong et al. reported that phthalocyanine analogues, tetra-2, 3-pyridoporphyrazine and its quaternized compounds have excellent properties compared to zinc phthalocyanine-type photosensitizer (Seotsanya-mokhosi, Kuznetsova et al., 2001). The amphiphilic phthalocyanine derivatives were concluded the best compound for a new generation of photosensitizers for PDT (Sakamoto, Kato et al., 2005).

The phthalocyanines are used as photosensitising agents which can be promoted to an electronically excited state by absorption of visible light wavelengths, thus promoting a sequence of photophysical, photochemical and photobiological events which result in the irreversible inactivation of a variety of biological systems (Miller, Baron et al., 2007) The phthalocyanines are used to enhance the phototoxic action through their association with carriers such as liposomes and peptides which favour their accumulation in target cells. The chemical structure provides the antimicrobial phototoxic action of phthalocyanines (Haywood-Small, Vernon et al., 2006).

2.2.1.3 Non-Linear Optics

In fact, following previous reports of cationic porphyrins as potential DNA-binding and cleavage agents, as well as sensitizers for PDT, is the first to report the synthesis of an octacationic pyridyl porphyrazine in 1999 (Villanueva, Caggiari et al., 1994 ; Anderson, Barrett et al., 1999). These novel systems underwent standard metallation reactions were both freely soluble in water as the chloride salt, and showed strong binding to calf thymus DNA (Anderson, Letsinger et al., 2000). In continuation of these studies, the synthesis of unsymmetrical pyridyl-substituted aminoporphyrazines was carried out. The resultant macrocycles displayed rich and varied redox chemistry and, therefore, show potential in the application to non-linear optics because of the presence of both donor and acceptor functionality (Fuchter, Beal et al., 2005). Recently, Bordbar and co-workers have reported the synthesis of tetracationic cobalt porphyrazines, with pyridine rings directly fused to the periphery (Bordbar, Davari et al., 2007). Open aperture Z-scan measurements have revealed that indium(III) porphyrazines are new nonlinear optical absorption (or reverse saturable absorption)

materials at 532 nm. Optical limiting (OL) studies have further demonstrated that they are potential materials in sensors or human eye protections at the same wavelength. Due to their high photostability and good solubility in common organic solvents, these compounds could also be promising materials for fabrication of practical solid optical limiters (Vagin, Yang et al., 2003). The phthalocyanine and porphyrazine materials are photostable and highly soluble in common organic solvents and they show good processability for solid optical limiter fabrication.

2.2.1.4 Chemical Sensors

In addition to the potential biomedical and non-linear optical applications of pyridyl-appended porphyrazines, it has been demonstrated that the synthesis of amino porphyrazines that bear pyridyl-based metal donor pockets (Beall, Mani et al., 1998). Such systems show efficient binding of four equivalents of a variety of metal cations including heavy metals such as cadmium(II) and, therefore, have potential in sensor applications. To further investigate the potential of pyridyl-mediated metal binding, and also reported the synthesis of a bipyridyl-appended porphyrazine (Fuchter, Beal et al., 2005). The dark conductivity changes which exposure to gases such as NO_2 and NH_3 cause to pthalocyanines in the form of thin films have also led to various chemical sensor studies (Mocker, Schmeisser et al., 1989 ; Snow, Barger et al., 1986). Under certain conditions photoconductivity changes (determined by the same interdigitated microcircuit arays used in the studies reported here), induced by the adsorption of gases, can exceed changes in dark conductivity, but the responses of the photoconductivity-based sensors are strongly dependent upon prior exposure to atmospheric O_2 (Pankow, Arbour et al., 1993). The complete synthesis and characterization of a new family of peripherally functionalized porphyrazines with four, three, or two (in a trans conformation) bis[thioethoxy(ethoxy)ethanol] moieties appended at the pyrroles has been shown to have applications as chemical sensors (Ehrlich, Skrdla et al., 2000). These “polyetherol” groups serve as weak exocyclic binding sites for a number of metal ions and also provide solubility of the porphyrazines in low molecular-weight alcohols and water. Modified porphyrazines exhibit distinct electronic spectral changes in the visible region (both absorbance and fluorescence) in response to treatment with Ag^+, Pb^{2+}, Cd^{2+}, Cs^+, and Ni^{2+} in solution. Such properties make these compounds intriguing candidates for incorporation into the transducer layers in optically based chemical sensors. The peripherally modified porphyrazines synthesized and spectroscopically

investigated represent a unique class of selective metal-ion chelators that absorb/emit in the visible region. Solubility in polar media (alcohols and water) aids the quantification of the metal−macrocycle interactions in solution that finds application in chemical sensors.

2.3 Porphyrin Complexes

Porphyrins and their reduced or otherwise modified derivatives are unquestionably the ligands par excellence of biology. The most common examples are the hemes (found in hemoglobins, myoglobins, cytochromes, catalases, and peroxidases), chlorophylls, and bacteriochlorophylls.Iron is the chelating metal found in hemes, and magnesium is found in the numerous chlorophylls and bacteriochlorophylls (Scheer). In more highly reduced tetrapyrrole-derived natural products, other metal ions are found; these include vitamin B_{12} (containing cobalt) and factor 430 (containing nickel). The mechanisms utilized in the mode of action of many tetrapyrrole metabolites often involve changes in the oxidation state of the central metal. Tetrapyrrole-derived macrocycles are able to accommodate the various oxidation state (and therefore metal ion size) changes due to the flexibility and adaptability of the basic chelating system. For the purposes of this treatise, only common routes to a number of very popular porphyrins will be discussed. Though methodology has been developed to enable the synthesis of the most complex porphyrins imagineable, discussion of the approaches to highly unsymmetrical natural porphyrins would be inappropriate to the organometallic focus of this volume (Kadish, Smith et al., 1999). Instead, the discussion will be mostly focused on the two most common porphyrin types; these are the peripherally octasubstituted porphyrins exemplified by 2,3,7,8,12,13,17,18-octaethylporphyrin (H_2OEP, (**1**)) and meso-tetrasubstituted systems such as 5,10,15,20-tetraphenylporphyrin (H_2TPP, (**2**)) (Fig. 2.5). Some variations on the themes of these two systems will also be mentioned; however, it should also be noted that, for example, porphyrin (**3**) and 2,3,7,8,12,13,17,18-octamethylporphyrin (**4**) (Fig. 2.6) are so insoluble in most organic solvents that they are rarely, if ever, used by porphyrin practitioners.

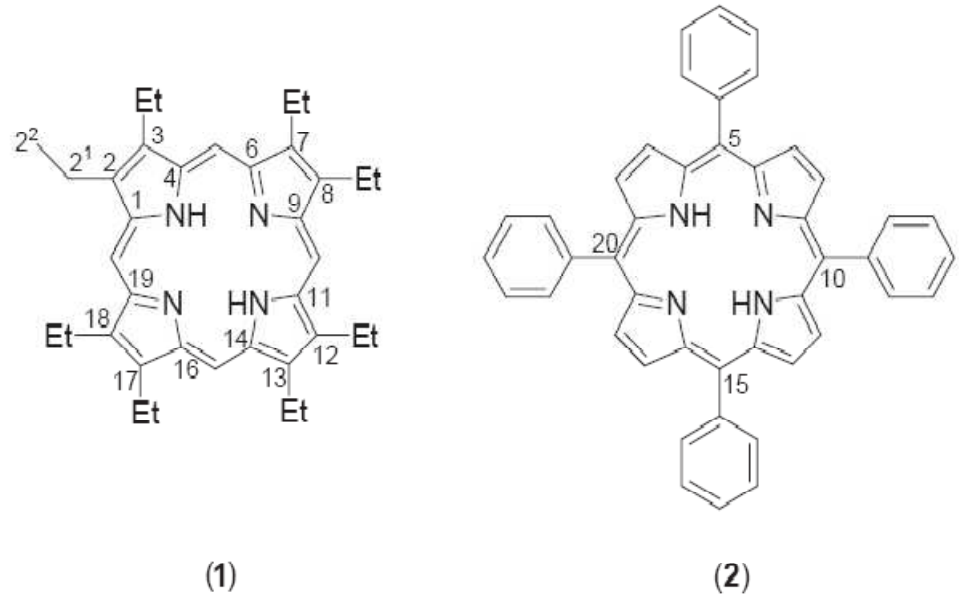


Figure 2.5 2,3,7,8,12,13,17,18-octaethylporphyrin H_2OEP, (**1**) and 5,10,15,20-tetraphenylporphyrin H_2TPP, (**2**).

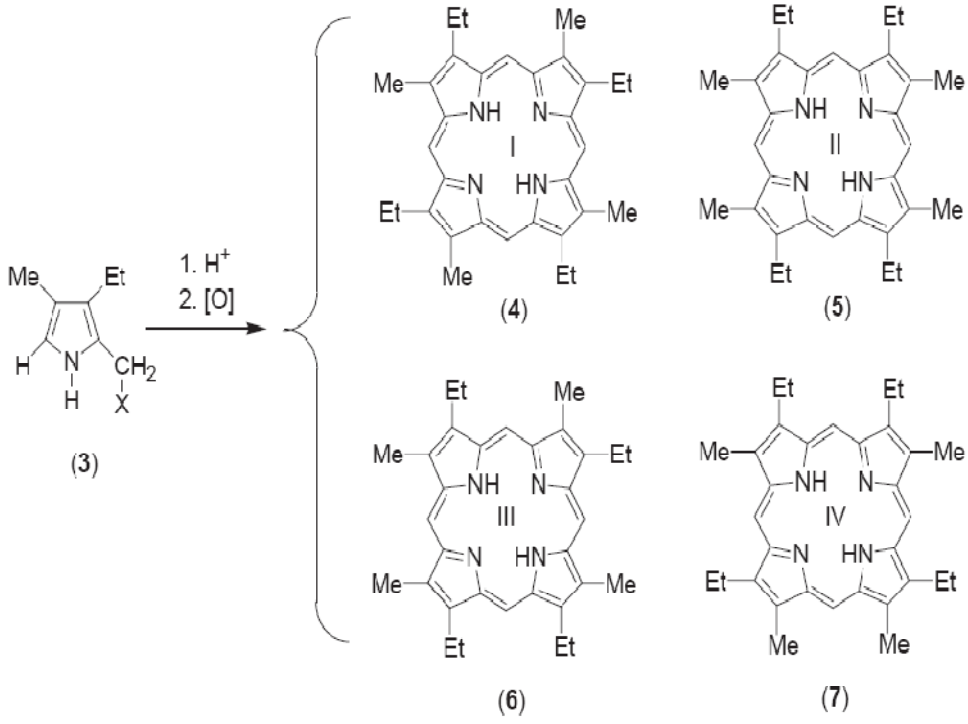


Figure 2.6 Porphyrin (**3**) and 2,3,7,8,12,13,17,18-octamethylporphyrin (**4**).

2.3.1 Acid Base Properties of Porphyrins

Quite valuable information on the structure of porphyrazines and their analogs can be obtained while studying their behavior in the proton donor media (Khelevina, Rumyantseva et al., 2004 ; Stuzhin, Khelevina et al., 1996). In addition, the possibility of practical application of porphyrazine metal complexes and their analogs significantly depends on their stability in solutions. In this connection, the study of the acid-base interactions of porphyrazines and their complexes is of interest in both theoretical and practical aspects.

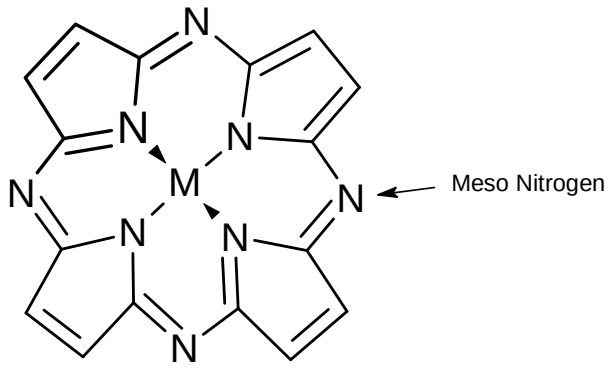


Figure 2.7 Porphyrazine metal complex.

Porphyrazines are weak multicenter conjugated bases. The number of porphyrazine donor centers involved in the acid–base interaction with acids, the character of the interaction, and the stability of the acidic forms obtained depend on the porphyrazine structure and the properties of the proton donor medium. The π orbitals of endocyclic N atoms in metal complexes of porphyrazines participate in formation of bonds with a central metal atom. Therefore, only the exocyclic meso-nitrogen atoms are involved in the acid–base interaction (Fig. 2.7). The long-wavelength region of the electronic absorption spectra of porphyrazine complexes in a neutral solvent contain intense Q-band due to the $\pi \rightarrow \pi^*$ electronic transitions $a_{1u} \rightarrow e_g^*$ of a macrocyclic ligand. The interaction of porphyrazines with acids is attended by the spectral changes in a visible region corresponding to the formation of different acidic-basic forms. In the case of porphyrazine complexes, the acid-base inter-actions occur in two stages, which are attended by bathochromic shift of the Q-band (Stuzhin and Khelevina, 1998; Khelevine, Romanenko et al., 2007).

$$MPz + H^+ <=> MPzH^+ \quad (2.1)$$

$$MPzH^+ + H^+ <=> MPzH_2^{2+} \quad (2.2)$$

The transfer of a proton from acid HA to base B: proceeds through the stages of formation of the acid associate, H-associate, ion–ion associate and fully ionized protonated form:

$$B: + HA <=> B^{\cdot}....HA <=> B^{\cdot} ....H....A <=> BH^+.... A^- <=> BH^+ + A^- \quad (2.3)$$

Acid associate H-assosiate Ion-ion associate Protonated form

The acidic forms thus obtained differ from one another in a degree of a proton transfer from the acid molecule to the donor center. In media with a low ionizing capability, the electron-donor centers of porphyrazine participate in a weak acid–base interaction and form H-associates and ion–ion associates. The complete transfer of a proton can be observed in strongly ionizing medium only (Petrov, 2001).

2.4 Application Field

The diversity of useful properties and structures of metalloporphyrins provides favorable conditions for varying the electronic states of the central metal atom which determines the coordination and catalytic properties, as well as searching for new effective catalytic systems that may be compatible with natural biocatalysts and even surpass them. We are speaking of synthesis, on the basis of porphyrin systems, of new effective catalysts, blood substituents, thermo- and photostabilizers, medicinal substances, organic semiconductors, pigments and dyes, solar cells, and inhibitors of homolytic degradation of protein molecules in living organisms exposed to X and gamma rays.

At present, natural porphyrins and their synthetic analogues are finding a host of industrial uses. Phthalocyanine which is a structural synthetic analogue of porphyrins, and its numerous intercomplex salts and functional derivatives are especially well known pigments.

Their extremely high thermal stability, fastness to light, inertness to acids and alkalis, insolubility in most solvents, high dyeing power, purity, and color intensity have ensured their reputation and wide application in the painting, printing, textile, and paper industries, as well as in chemical fiber and plastic dyeing processes, as superior quality blue, blue-green, and green pigments. Also used as pigments are high-chlorine derivatives of phthalocyanine and its complexes (e.g. “phthalocyanine green”, which contains up to 15 chlorine atoms in the copper-phthalocyanine nucleus). Sulpho derivatives of copper phthalocyanine are employed as valuable direct dyes for cotton, known as “Sirius turquoise” and “direct light-fast turquoise”. In addition to the most widely used copper complex, complexes of phthalocyanine with Co, Ni, Al, and other metals are also used industrially.

The introduction of various functional substituents into the benzene nuclei of phthalocyanine, whereby it acquires solubility, new chromophore properties, and the ability to be fixed on fibers from solution, permits numerous dyes of different classes to be obtained on its basis.

A popular process in the textile industry is phthalogenic dyeing of fabrics, based on synthesis of phthalocyanines from intermediate products (so called phthalogens) directly on fibers.

Broad possibilities for using porphyrin complexes are being opened up in the technology of semiconductors and lasers, as well as in quantum-electronics research, because of their exhibition of semiconductor and other valuable properties.

Another promising area of their application as oxidation-reduction catalysts includes industrial synthesis, enzyme catalysis, and electrochemical processes involved in the catalytic reduction of oxygen in fuel cells. Other uses of phthalocyanines include, for example, processes for producing heavy isotopes of some elements and oxidation-reduction indicators.

CHAPTER 3

SYNTHESIS METHODS OF PORPHYRAZINE COMPLEXES

3.1 General Synthesis Methods

The porphyrazine ring has amphoteric properties, which in acidic media acts as a base due to μ-nitrogen atoms, while in basic media it results in acidic properties due to ionization of central imino groups (Fig. 3.1). The basic Porphine (PH_2) from which porphyrazine ring derived forms complexes with many metals of various groups of the Periodic system of elements. Various methods for the preparation of metal-porphyrazine complexes (MPA) from other porphyrazine derivatives or 1,2-dicyanoethenes are known (Fischer and Endermann, 1937 ; Zhao, 2004). These methods include (**a**) fusion of ethene-1,2-dicarbonitriles with metals or their salts, sometimes in the presence of urea; (**b**) boiling of solutions of ethene-l,2-dicarbonitriles with metals, their salts, or alkoxides (for example, magnesium alkoxide), often in the presence of a catalyst (for example, ammonium molybdate); (**c**) boiling of an (PH_2) solution with metal salts; and (**d**) boiling of solutions of labile metal complexes of porphyrazine (for example, magnesium complex) with metal salts.

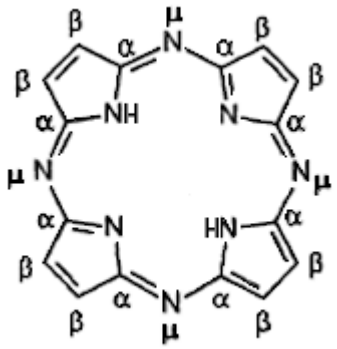


Figure 3.1 Positions for a porphyrazine molecule.

One of the synthesis methods of porphyrazines is tetramerization of pyrrole derivatives by analogy with the known synthesis of porphyrins, namely: by reaction of 4-ethyl-3-methylpyrrole with bromine and ammonia or by treatment of 4-ethyl-3-methylpyrrole-2,5-diisocyanate with a mixture of pyridine and tetramethylammonium hydroxide. However, tetraethyltetramethyl-porphyrazine has been obtained only in low yields (Fig. 3.2) (Linstead and Whalley, 1952 ; Baguley, France et al., 1955).

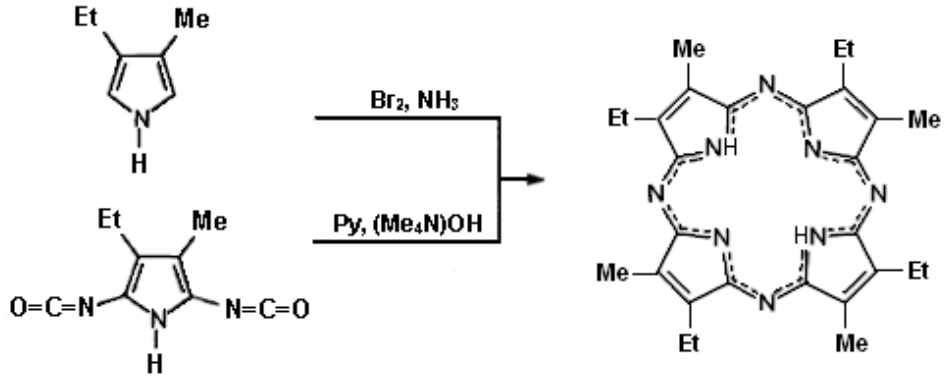


Figure 3.2 Synthesis of porphyrazine by tetramerization of pyrrole derivatives.

The existing methods for synthesizing porphyrazine are based on the tetramerization of derivatives of the corresponding 1,2-dicarboxylic acids, maleonitriles (Z-1,2-dicyanoethenes), or their adducts with ammonia, 2-amino-5-iminopyrrolenines. The cyclic system is initially closed to form dehydro-porphyrazine, which then is reduced to porphyrazine under the reaction conditions.

In 1952, Linstead reported a general approach to porphyrazine macrocyclization, using magnesium alkoxide and maleonitrile reagent to synthesize the unsubstituted porphyrazine (Fig. 3.3). This is still the only widely used method for porphyrazine formation since then. Cyclotetramerization (Fig. 3.4) of the maleonitrile reagent(s) templated by a divalent magnesium ion results in the formation of porphyrazine products that contain a magnesium ion in the central cavity. Magnesium porphyrazines are easily demetallated under acidic conditions to form the free-base porphyrazine ligand, which subsequently can be complexed to a plethora of metallic centers.

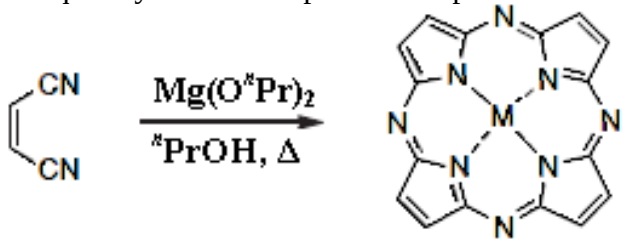


Figure 3.3 Cyclotetramerization of the maleonitrile reagent.

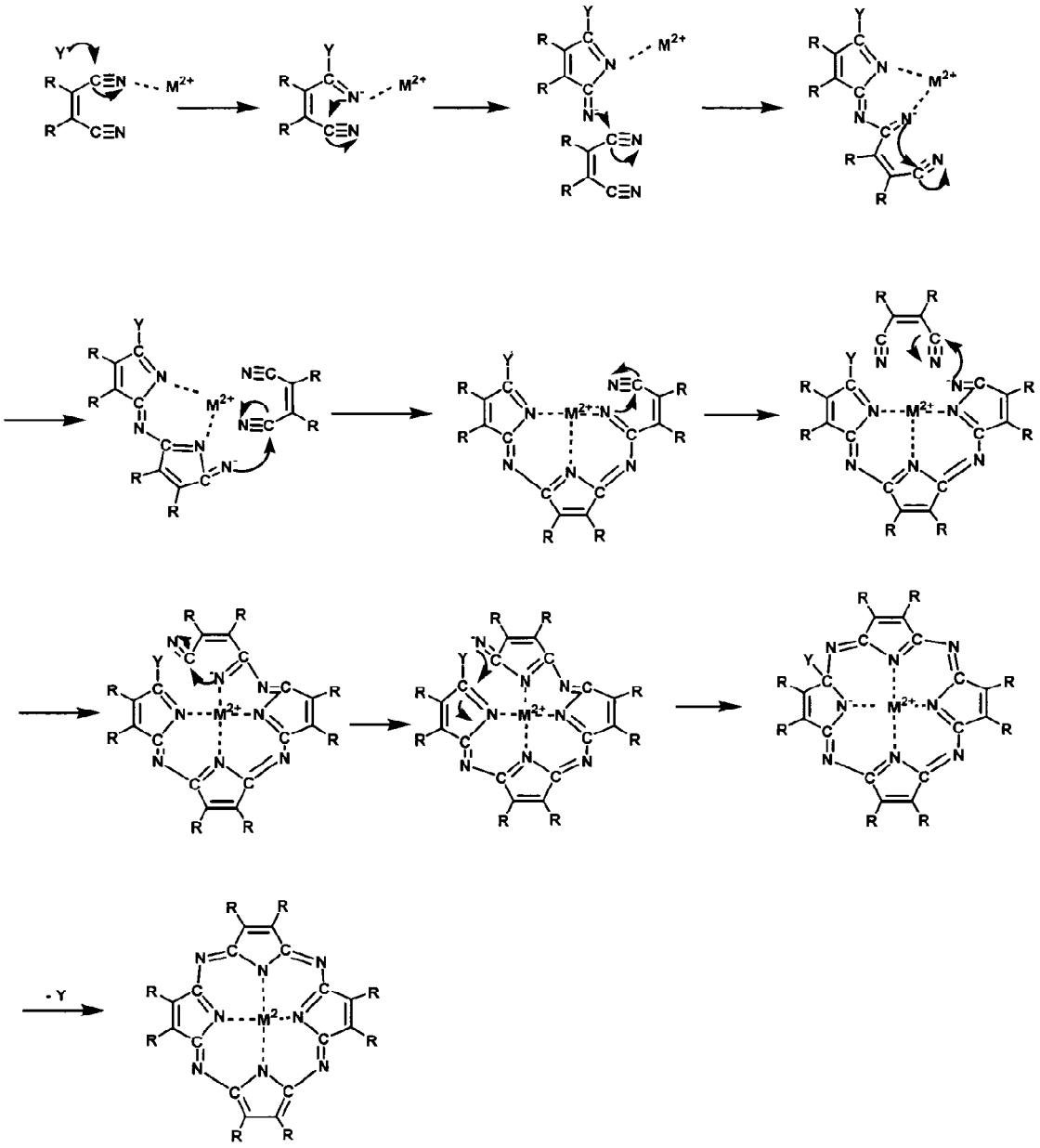


Figure 3.4 Possible mechanism for porphyrazine cyclization.

According to the studies by Ercolani and coworkers, it has come out that the magnesium is not the only template available in the synthesis of the porphyrazine macrocycles (Donzello, Dini et al., 2003). They used NaOEt and LiOAm instead of magnesium alcoholate to synthesize annulated diazepine ring fused porphyrazines. Thus, they demonstrated that sodium(I) and lithium(I) could also act as templates to produce the sodium ($PzNa_2$) or lithium ($PzLi_2$) porphyrazines respectively, in good yields. Besides, the lability of these counter cations was exploited by performing direct metal-exchange reactions (rather than by demetallation) to produce Mn^{2+}, Co^{2+}, Cu^{2+},

and Zn^{2+} complexes. However, it has been found that these methods less effective for the electron-rich aminomaleonitrile reagents although they are efficient for the diazepino maleonitrile starting materials.

Additionally, there has been reported another method by Chandrasekharam and coworkers, a onepot synthesis of metalloporphyrazines from maleonitrile starting materials with hexamethyldisilazane (HMDS), catalytic amount of *p*-toluenesulfonic acid and a metal template (ZnX_2, MgX_2, CuX_2, NiX_2, etc.). They used this method to produce amino-, thio-, and phenyl group including pophyrazines, and by using accelerating effect of microwave irradiation on the tetramerization, they could overcome long reaction time (10-24 h) problem (Chandrasekharam, Rao et al., 2007).

Recently, Hofmann and his coworkers have synthesized a highly polar unsymmetrical porphyrazine on a large scale, with minimal chromatographic purification by employing a novel-one pot, 3-step sequence (Guinchard, Fuchter et al., 2007). According to the method, two maleonitrile precursors, one of which was present as a mixture of *E*- and *Z*-isomers, were transformed, via the corresponding pyrroline diimine, into the target porphyrazine and its *seco*-porphyrazine derivative, which is under exploration as a targeted photodynamic therapeutic agent.

3.2 Transition Metal Complexes of Porphyrazines

The porphyrazine macrocycle is a good ligand to most metals even though only few porphyrazine metal complexes have been reported compared to their phthalocyanine and porphyrin counterparts, where most research in this area has been centered. This is because porphyrazines still represent a new field of research, with much research based on the selective incorporation of substituents. Even though metallations can be effected as an integral part of their synthesis, such as in cases in which the macrocyclisation in the presence of a templating transition metal salt or Li or Mg alkoxides, the best method that gives a product of high purity is the metallation reaction of a free-base ligand (Choi, Tsang et al., 2004 ; Antipas, Dolphin et al., 1978).

It has been already determined that a metal in the centre, or metal complexes to peripheral ligating groups can alter the physical and chemical properties of a porphyrin,

phthalocyanine or porphyrazine (Antipas, Dolphin et al., 1978 ; Nevin, Liu et al., 1987). When the central metal is iron or cobalt, phthalocyanines make good electrocatalysts for the reduction of oxygen at a fuel cell cathode (Leznoff, Marcuccio et al., 1985). It has also been shown that iron (II) porphyrins decompose oxygen through a mechanism involving two porphyrins acting on oxygen molecule. Metal porphyrins have been also shown to catalyze carbene-type transformations with diazo reagents such as cyclopropanation of alkanes and C-H insertion of alkanes. Recently, it has been reported that iron (II) porphyrin complexes can catalyse the olefination of a selection of aldehydes with diazoacetate in the presence of triphenylphosphine (Chen, Huang et al., 2003). With porphyrins, phthalocyanines and porphyrazines as photodynamic therapy agents, a metal in the centre may improve their photosensitivity, especially in the instances of the diamagnetic metals like zinc (Ogunsipe, Chen et al., 2004).

The normal charge of a porphyrin, porphyrazine or phthalocyanine is (-2). Therefore, the metal ion to be accepted in order to form a stable complex is the one with a (+2) charge. Metal ions with a charge of (+1), requires an additional ion with (+1) charge (Fig.3.5) (Leznoff, Marcuccio et al., 1985).

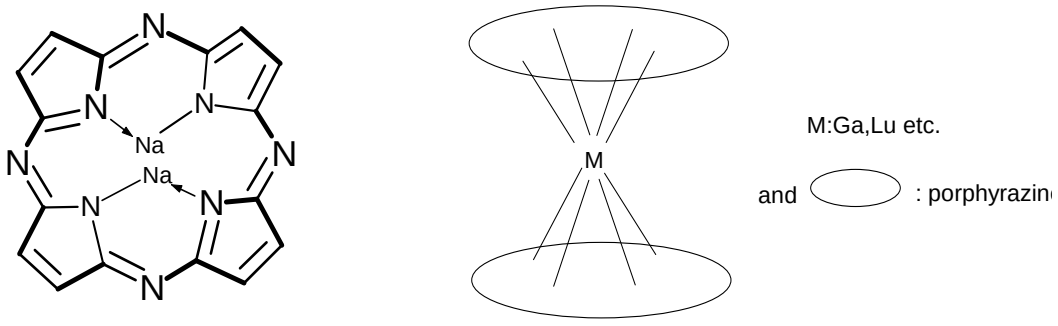


Figure 3.5 Metal complex formation of porphyrazine.

Metal ions with a charge of (+3) or higher require additional “axial” ligands. In the case of larger ions, the phthalocyanine or porphyrazine or porphyrin cannot fully accommodate these ions within the core cavity and in this case the metal becomes surrounded by two phthalocyanines, porphyrins or porphyrazines, making a “sandwich” complex (Fig. 3.5) (Leznoff, Marcuccio et al., 1985).

Metalation in phthalocyanine and porphyrazine compounds can be incorporated into the synthesis as shown in Figure 3.6 (Chen, Huang et al., 2003). In a metal-free

porphyrazine (**1**), central metallation is mostly done by heating from 50 ºC to reflux the metal-salt [Ni(OAc_2), $MnCl_2$, etc.] in a mixture of chlorobenzene and DMF or in neat DMF. Peripheral metallation can be effected by heating the porphyrazine in a suitable solvent mixture (mostly using acetonitrile-trichloromethane) (Uchida, Reddy et al., 2003).

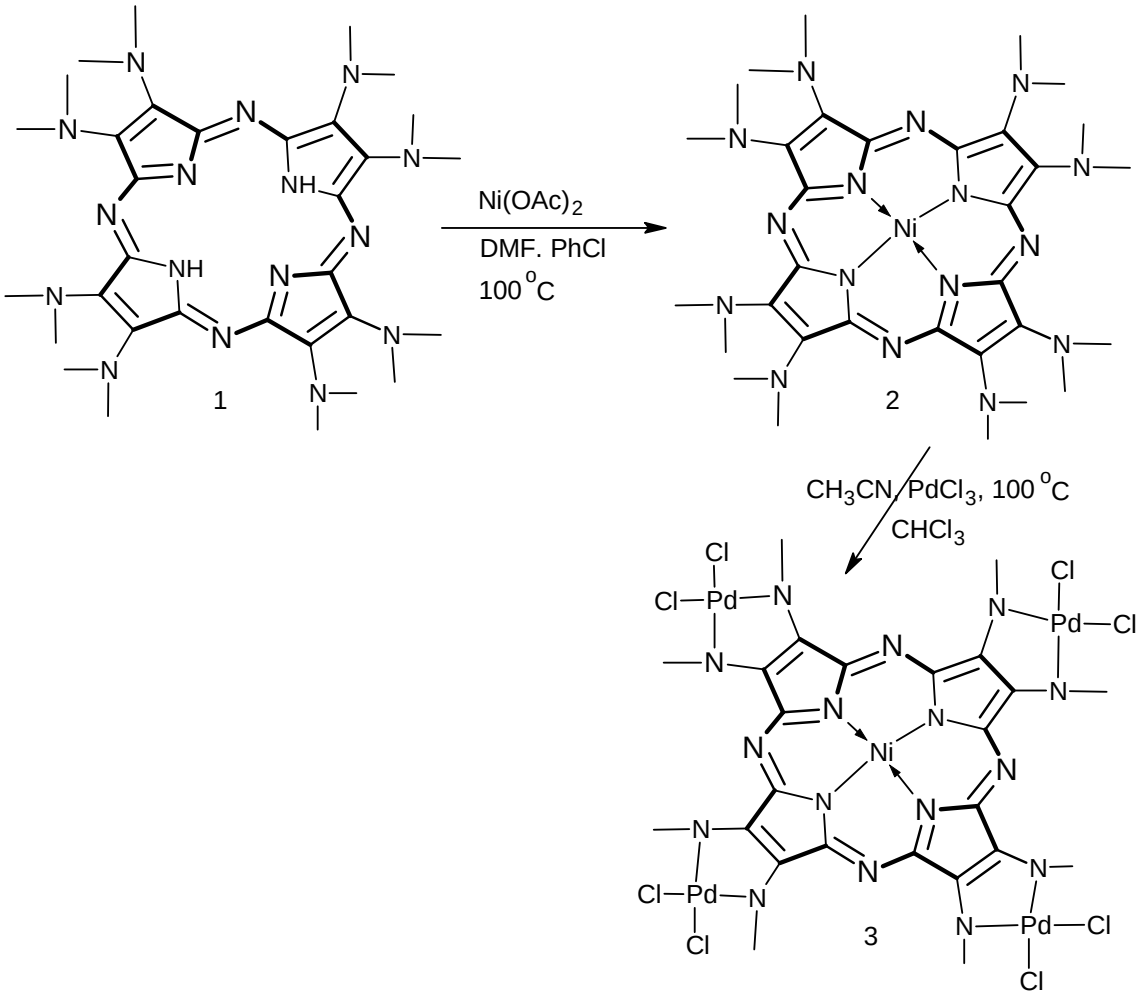


Figure 3.6 The synthesis of metal complex of porphyrazine **2** with Ni (central) and Pd (peripherally) metals **3**.

If the starting porphyrin contains etherified carboxyl groups, for example H_2MP DME or H_2PP DME, etherification and chromatographic separation on a column are required after complex formation under stringent conditions, in some cases with subsequent recrystallization. Such procedures are described for vanadyl mesoporphyrin synthesized from H_2MP DME and VCl_4 in a scaled glass tube at 165 °C for Mn^{3+} mesoporphyrin synthesized from mesoporphyrin hydrochloride and $MnAc_2$ in glacial

HAc with admission of air, and by other investigators.

Many metals form metalloporphyrins with different degrees of oxidation of the central atom. They include Fe^{2+}-Fe^{3+}, Co^{2+}-Co^{3+}, Ag^{+}-Ag^{2+}, Mn^{2+}-Mn^{3+}-Mn^{4+}, Sn^{2+}-Sn^{4+}, Cr^{2+}-Cr^{3+}. The least stable of all are Fe^{2+}, Mn^{2+}, Ag^{+}, Cr^{2+} and Sn^{2+} porphyrins. Cobalt usually yields complexes in the form of Co^{2+}; special oxidation conditions are required for it to become Co^{3+}. However, some porphyrins promote oxidation in air; for example, protoporphyrin with $MnAc_2$ and $CoAc_2$ in hot glacial HAc forms (HO)MnPP and (HO)CoPP in the presence of HCl and air.

A complex of mesoporphyrin DME with Co^{2+} prepared in methanol turns to (HO)CoMP when kept in air. The metal oxidation process is catalyzed with olefins and acetylenes.

3.3 Porphyrazines That Bearing Different Substituents

Novel metallo-porphyrazines substituted with dimethylaminoethylthio, crown ether, 1-naphthylmethylthio, 4-*tert*-butylphenylthio, 9-anthracenylmethylthio ect. have been described in this section. These novel compounds have been characterized by elemental analysis, together with FT-IR, ^{1}H NMR, UV-Vis and mass spectral data.

3.3.1 Octakis(1-naphthylmethylthio) Substituted Porphyrazine Derivatives

Magnesium porphyrazinate substituted with eight (1-naphthylmethylthio)groups on the peripheral positions has been synthesized by cyclotetramerization of 2,3-bis(1-naphthylmethylthio)maleonitrile in the presence of magnesium butanolate. The metal-free derivative was obtained by its treatment with trifluoroacetic acid and further reaction of this product with copper(II) acetate, zinc(II) acetate and cobalt(II) acetate led to the metal porphyrazinates (M=Cu, Zn, Co) (Fig. 3.7) (Gonca, Köseoğlu et al., 2004).

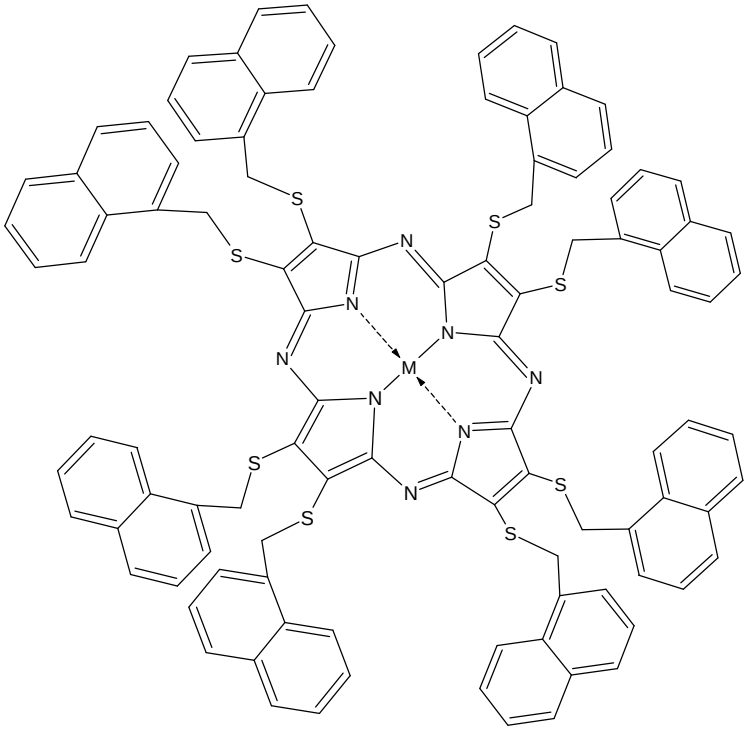
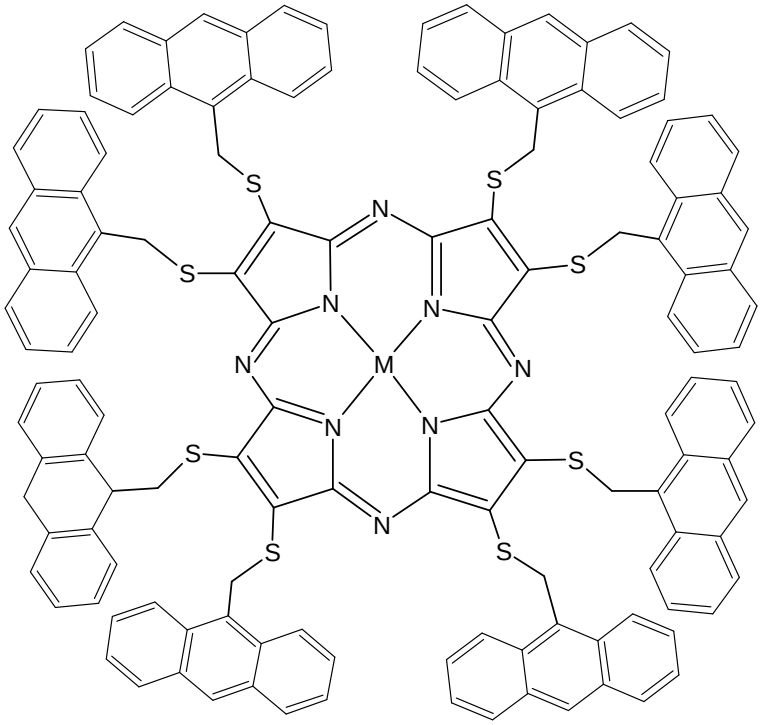


Figure 3.7 Octakis (1-naphthylmethylthio) substituted porphyrazines (M=Mg; 2H; Cu; Zn; Co).

3.3.2 Octakis-(9-anthracenylmethylthio) Substituted Novel Porphyrazines

A magnesium porphyrazinate carrying eight (9-anthracenyl) units on the periphery through flexible methylthio bridges has been synthesized by cyclotetramerization of 3,4-(9-anthracenylmethylthio) pyrroline-2,5-diimine (Fig. 3.8) in the presence of magnesium butanolate. The metal-free derivative was obtained by treatment with trifluoroacetic acid and further reaction of this product with copper(II) acetate, zinc(II) acetate, and cobalt(II) acetate led to the metal porphyrazinates (M^{2+}= Cu^{2+}, Zn^{2+}, Co^{2+}) (Gonca, 2008).



M= Mg (**4a**); 2H (**4b**); Cu (**4c**); Zn (**4d**); Co (**4e**)

Figure 3.8 Octakis(9-anthracenylmethylthio)substituted porphyrazines.

UV-Vis spectra of porphyrazine core are dominated by two intense bands, both correlated to $\pi \rightarrow \pi^*$ transitions (van Nostrum and Nolte, 1996 ; Pullen, Faulmann et al., 1999). The presence of an electron donating group on the periphery causes a bathochromic shift on Q bands. UV-Vis spectra of metallo porphyrazines (**4a, 4c-e** in $CHCl_3$) prepared in this present work exhibited intense single Q band absorption of the $\pi \rightarrow \pi^*$ transitions around 648-656 nm and B bands in the UV region around 344-352 nm. For the metal-free derivative (**4b**), the Q band is split into two peaks at 624 and 680 nm as a consequence of the change in the symmetry of porphyrazine core from D_{4h} (in the case of metallo derivatives) to D_{2h} (Fig. 3.9). Here, in the case of porphyrazines with appending (9-anthracenylmethylthio) substituents in addition to these absorptions of the porphyrazine core, an intense absorption due to the $\pi \rightarrow \pi^*$ transition of anthracene groups appeared for all these porphyrazines derivatives (**4a-e**) in the UV region at about 284-288 nm (Gonca, Köseoğlu et al., 2004 ; Yenilmez, Özçeşmeci et al., 2004). An absorbance vs concentration study indicated that due to the bulky anthracene substituents, no aggregation occurred for (**4a***).*

In conclusion, novel porphyrazines surrounded with eight bulky anthracenylmethylthio units have been described; high electron density on the substituents resulted in a second absorption in the ultraviolet region of comparable intensity as the intense B band of porphyrazines.

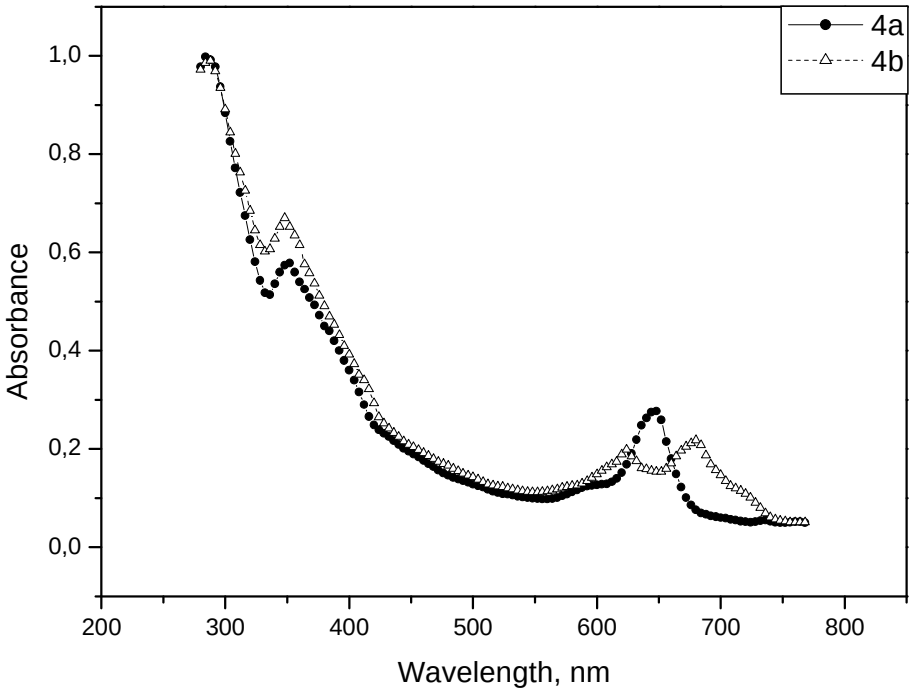


Figure 3.9 UV-Vis spectra of (**4a**) and (**4b**) in chloroform.

3.3.3 Octakis (9-anthracenylmethylthio) Iron Porphyrazine Derivatives

Chloro[octakis(9-anthracenylmethylthio)porphyrazinato]iron(III), [FePzCl] (Fig. 3.10), was prepared by the reaction of metalfree porphyrazine with iron(II) acetate and further treatment with HCl solution. The monomeric bisaxial complex [FePz$(py)_{2}$] as well as the bridged complex [FePz$(pyz)]_n$ (Fig. 3.11) were formed as stable complexes by reacting [FePzCl] with pyridine or pyrazine, respectively (Gonca, 2008).

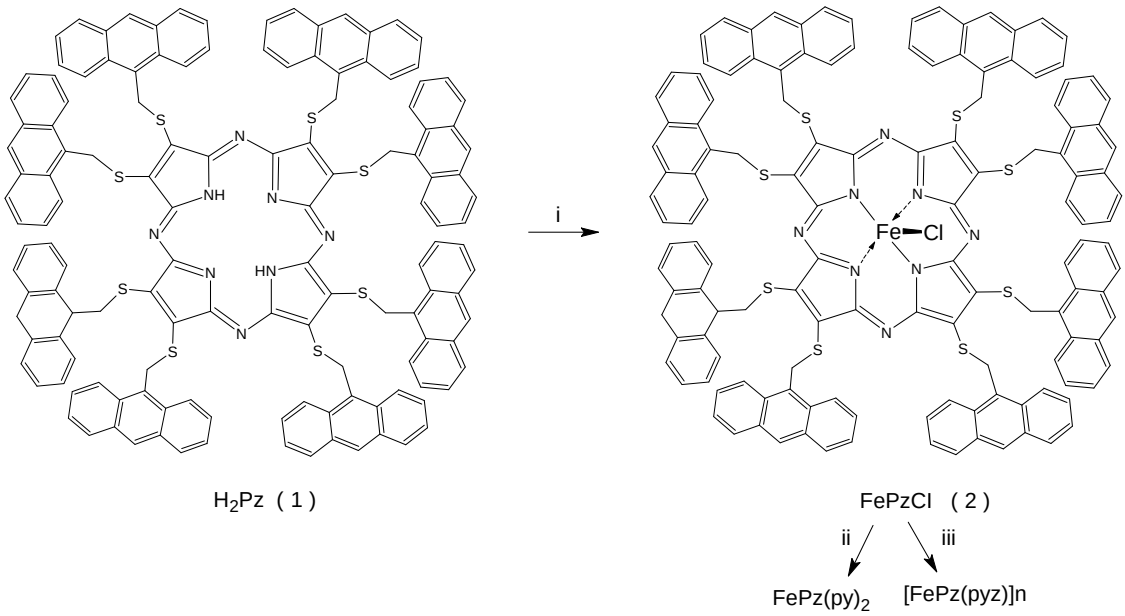


Figure 3.10 Synthesis route to new compounds: (**i**) $Fe(OAc)_2$, acetic acid, HCl; (**ii**) pyridine; (**iii**) pyrazine.

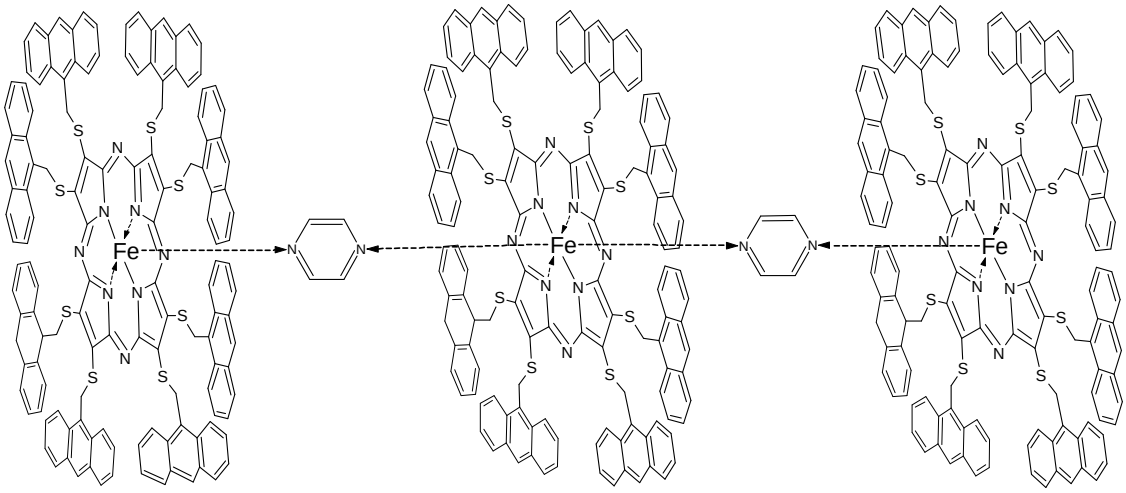


Figure 3.11 μ-Pyrazine[octakis(9-anthracenylmethylthio)porphyrazinato]iron(II) $[FePz(pyz)]_n$.

3.3.4 Porphyrazines with Tosylamine Functional Groups

Metal-free and metallo-porphyrazines (M= Mg, Ni and Co) carrying eight functional tosylaminoethylthia- groups on peripheral positions have been synthesized for the first time from cyclotetramerization of 1,2-bis (2-

tosylaminoethylthia)maleonitrile in the presence of magnesium propoxide; the metal-free derivative was obtained by treatment of with trifluoroacetic acid and it was further converted into Co(II) and Ni(II) derivatives by using acetate salts of corresponding metal ions. The reactivity of tosylamino-groups was verified by its alkylation to yield octakis[(tosyl)(hexyl)amino-ethylthia]porphyrazinatomagnesium(II) (Fig. 3.12) (Uslu and Gül, 2000).

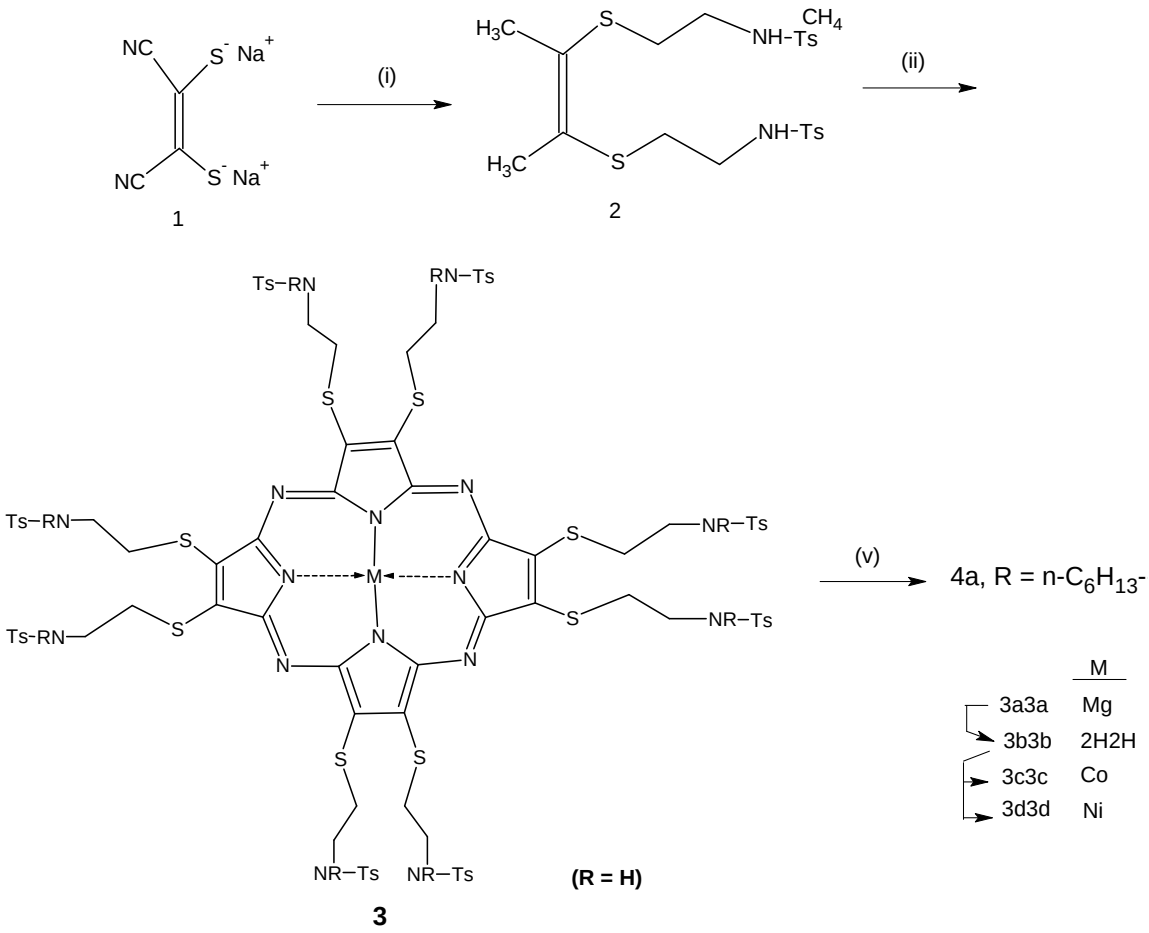


Figure 3.12 Synthesis route to novel porphyrazines. (**i**) di(tosyl)aminoethanol; (**ii**) magnesium, I_2 propanol; (**iii**) trifluoroacetic acid; (**iv**) cobalt(II) acetate or nickel(II) acetate; (**v**) *n*-hexylbromide.

The electronic absorption spectra of all the metallo porphyrazines **3a**, **3c**, **3d** and **4a** exhibit a strong absorption between 647–670 nm which is due to a p→p* transition and is commonly referred to as Q band. A second intense and broad p→p* transition in the range 343–374 nm which is called Soret or B band is also a characteristic of these tetrapyrrole derivatives (Fig. 3.13). As expected, the metal-free derivative **3b** shows a

splitted Q band because of the change in symmetry from D_{4h} in metallo-species to D_{2h} in metal-free ones. Aggregation of symmetrical porphyrazines and phthalocyanines can be efficiently followed from band broadening to a blue shift of the Q bands. However, spectra recorded of 10^{-4} and 10^{-5} M solutions of porphyrazines **3a**, **3b**, **3c**, **3d** and **4a** in chloroform are identical in shape, implying that aggregation is not very effective in the present case. This might be attributed to the bulky nature of the substituents which prevent the interactions between porphyrazine cores at least in these concentrations. Similarly, negligible differences between the spectra obtained in different solvents (chloroform, dichloromethane and acetone) can be also taken as a further confirmation of this proposal.

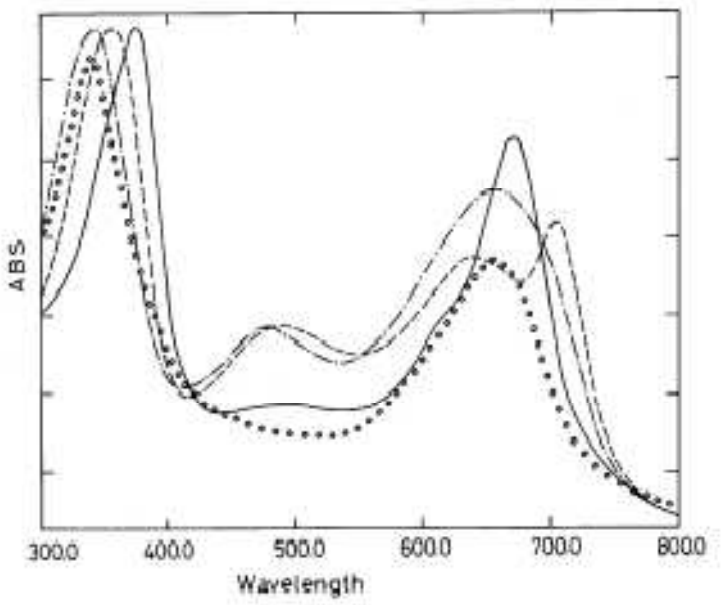
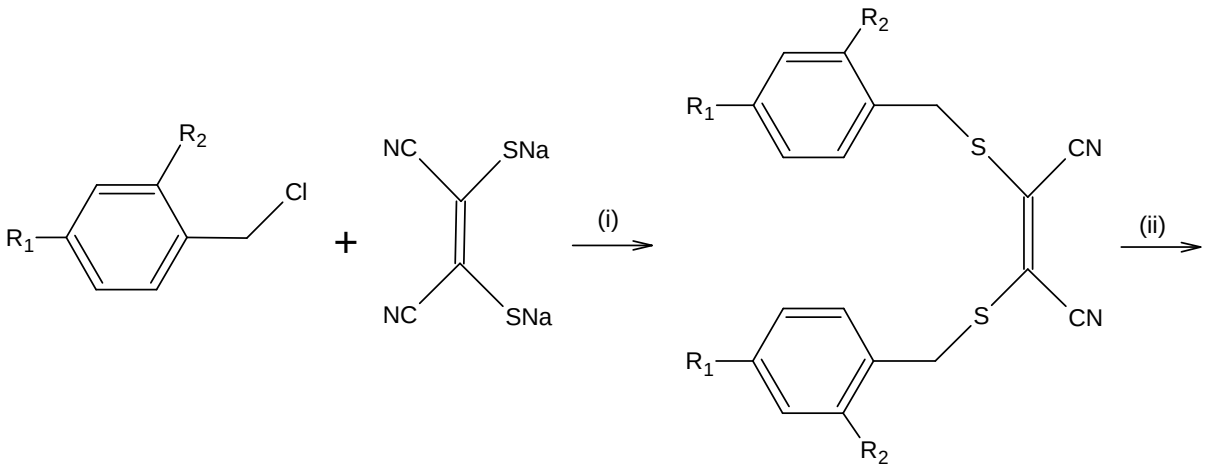


Figure 3.13 Electronic spectra of porphyrazines in chloroform. (—), **3a**; (---), **3b**; (**…**), **3c**; (-·-·-·),**3d**.

In conclusion, new porphyrazine derivatives with reactive tosylamino groups on the periphery was synthesized and demonstrated that this reactive site can be used to prepare diverse macromolecules based on porphyrazines.

3.3.5 Porphyrazines with Eight (*p-tolylmethylthio*) and (*o-tolylmethylthio*) Units

By cyclotetramerization of 1,2-bis(*p*-tolylmethylthio) maleonitrile and 1,2-bis(*o*-tolylmethylthio) maleonitrile in the presence of magnesium butanolate, magnesium porphyrazinates carrying eight (*p*-tolylmethylthio) and (*o*-tolylmethylthio) units on the periphery positions have been synthesized. The conversions of magnesium porphyrazinates into the metal-free derivatives were achieved by the treatment with relatively strong acids (e.g. trifluoroacetic acid). Further reactions of these products with copper(II) acetate, zinc(II) acetate and cobalt(II) acetate have led to the metal porphyrazinates (M^{2+}= Cu^{2+}, Zn^{2+}, Co^{2+}). The new compounds were characterized by elemental analysis, together with FT- IR, ^{1}H NMR, UV-Vis and mass spectral data (Cenan and Gonca, 2008).



(R_1: CH_3, R_2: H) **2** (R_1: CH_3, R_2: H)

(R_1: H, R_2: CH_3) **3** (R_1: H, R_2: CH_3)

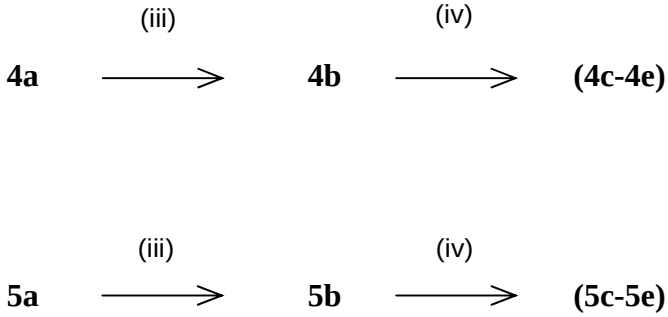
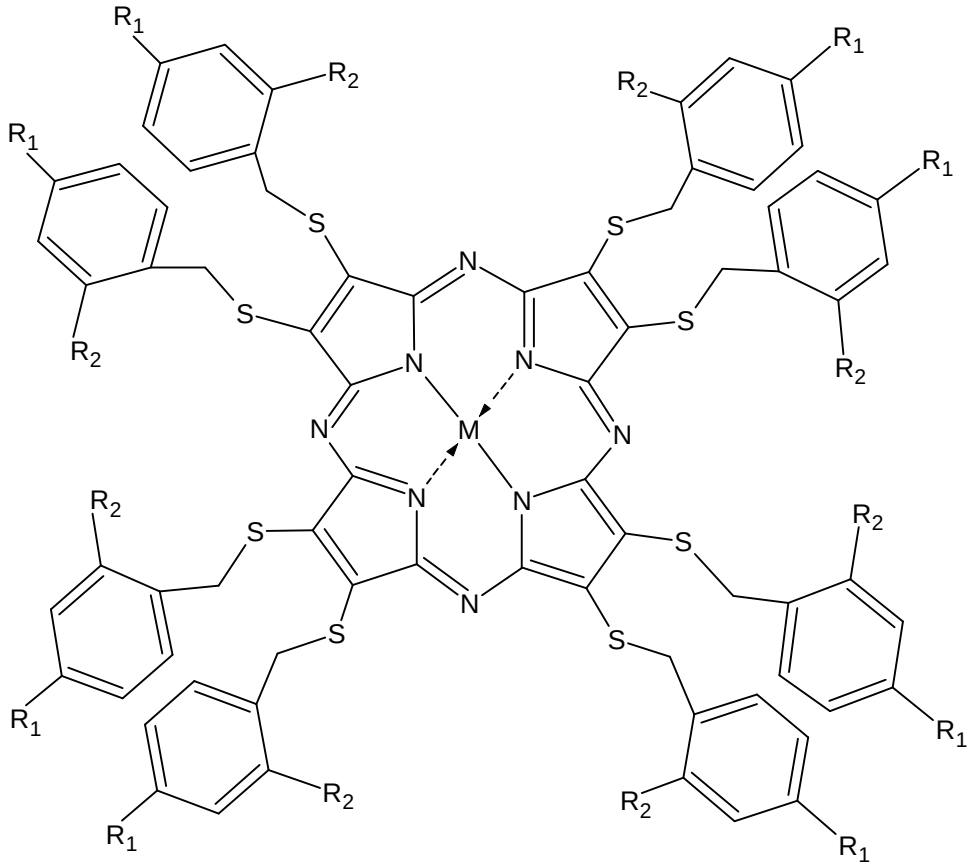


Figure 3.14 (**i**) Methanol; (**ii**) Mg turnings, I_2, n-BuOH; (**iii**) CF_3CO_2H; (**iv**) EtOH and $Cu(OAc)_2$, $Zn(OAc)_2$, or $Co(OAc)_2$.



(4a-e) (R_1: CH_3, R_2: H)

(5a-e) (R_1: H, R_2: CH_3)

M = (Mg, 2H, Cu, Zn, Co)

Figure 3.15 Octakis(*p*-tolylmethylthio) substituted porphyrazines (**4a-e**) and octakis(*o*-tolylmethylthio) substituted porphyrazines (**5a-e**).

Electronic spectra are especially useful to establish the structure of the porphyrazines (**4a-e, 5a-e**). UV-Vis spectra of porphyrazine core are dominated by two intense bands, the Q band around 650 nm and the B band in the near UV region around 350 nm, both correlated to $\pi \rightarrow \pi^*$ transitions. The presence of an electron-donating unit on the periphery causes a bathochromic shift on Q bands. The UV-Vis spectra of porphyrazines (**4a, 4c-e, 5a, 5c-e** in chloroform) prepared in the present work exhibited intense single Q band absorption of the $\pi \rightarrow \pi^*$ transitions around 642-675 nm and B bands in the near UV region around 345-378 nm. As a consequence of the change in the symmetry of porphyrazine core from D_{4h} (in the case of metallo derivatives) to D_{2h}, the electronic absorption spectra of **4b** and **5b** display a split in the Q band at 634 and 706 nm and at 638 and 715 nm, respectively. UV-Vis spectra of **4a** and **4b** in chloroform are

shown in Fig. 3.16. An absorbance *vs.* concentration study indicated that due to the bulky (*p*-tolylmethylthio) and (*o*-tolylmethylthio) substituents, no aggregation occurred either for **4a**, **4b**, **5a** or **5b**.

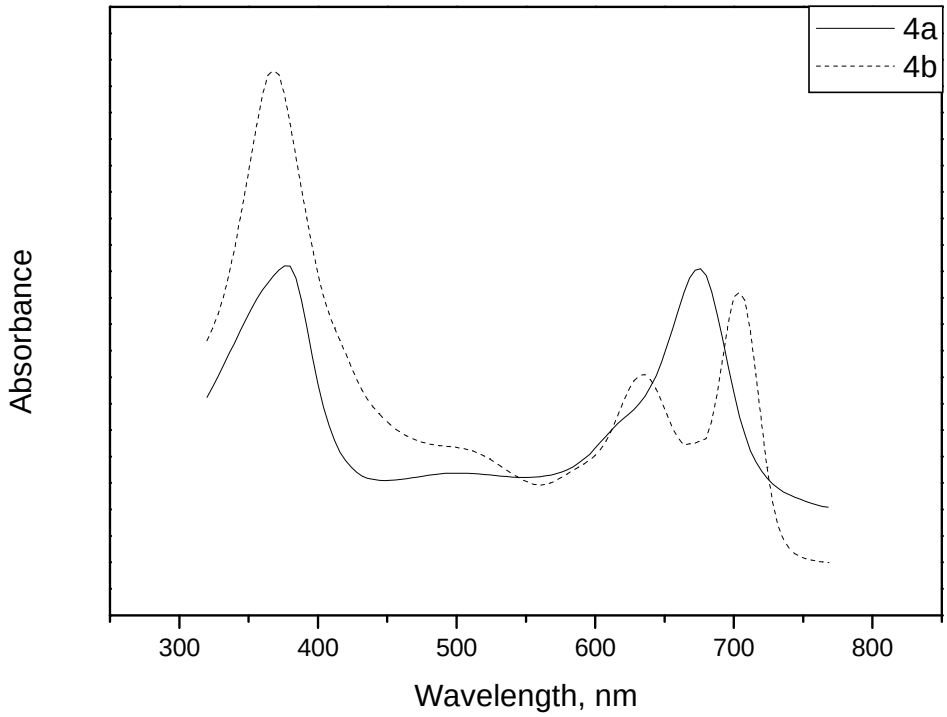


Figure 3.16 UV-Vis spectra of **4a** and **4b** in chloroform

3.3.6 Magnesium Porphyrazinate with Eight Triphenylphosphonium Moieties Attached Through (2-Sulfanyl-Ethoxycarbonyl-2-Propyl) Bridges

A new magnesium porphyrazinate with eight [triphenyl-(2-sulfanyl-ethoxycarbonyl-2 propyl)phosphonium]bromide groups has been prepared from octakis (2-hydroxyethylthio)porphyrazinatomagnesium and (2-carboxy-1-methylethyl) triphenylphosphonium bromide {[$(Ph)_3PCH_2CH(Me)CO_2H$]Br}(Fig.3.17) (Gonca and Gül, 2005).

The aim of this work has been to synthesize a novel porphyrazine structure carrying phosphorous containing groups on the periphery. The phosphoniumyl porphyrazine has eight positive charges in the periphery of the p-plane of the tetrapyrrole core. The cationic sites are separated from one another by the porphyrazine

unit together with the ester bridges. Thus, these octa-cationic structures are totally different from the cationic porphyrazine derivatives whose cationic centers can influence the electron density by inductive effect.

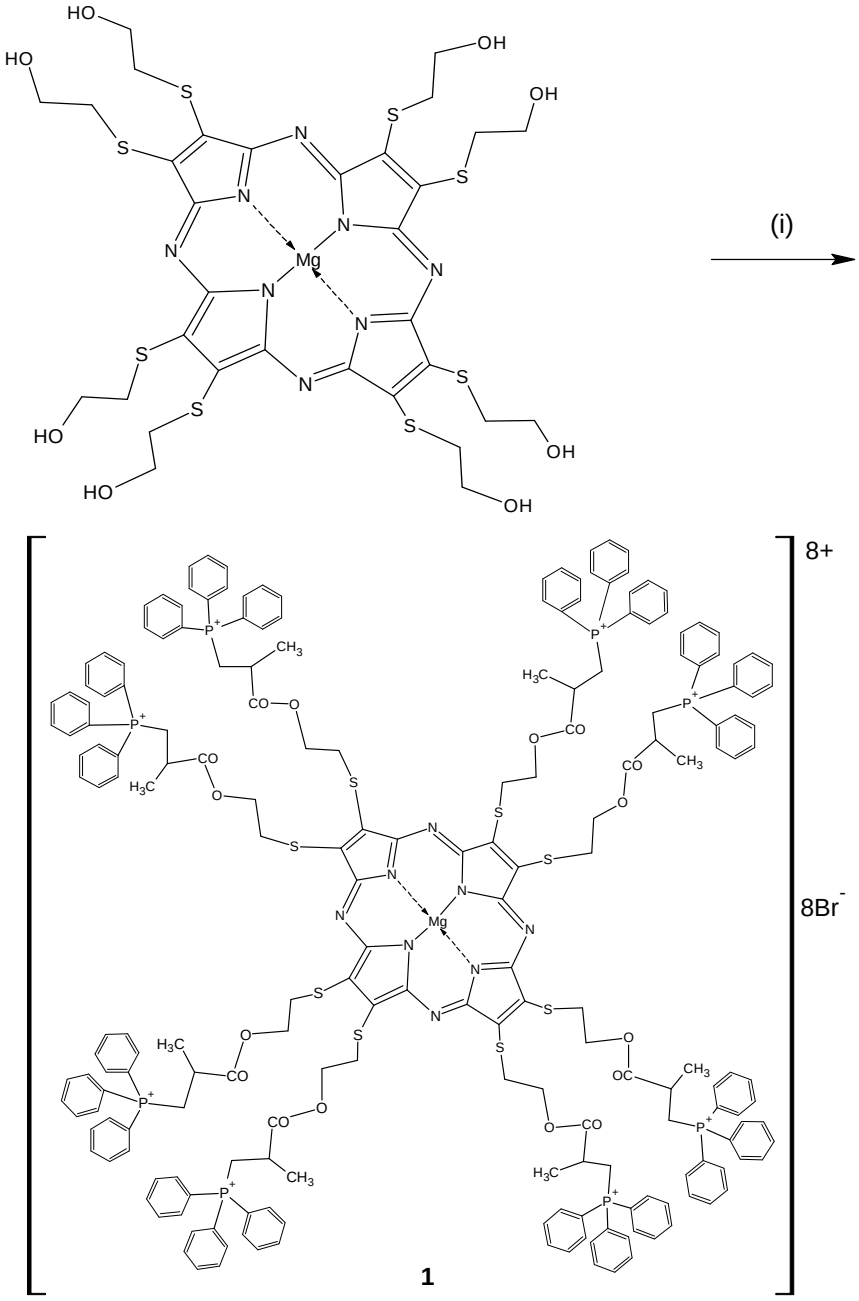


Figure 3.17 (**i**) [$(Ph)_3PCH_2CH(Me)CO_2H$]Br, DCCI, toluene-*p*-sulfonic acid and dry pyridine. {Octakis[triphenyl-(2-sulfanyl-ethoxycarbonyl-2-propyl) phosphonium]yl- porphyrazinatomagnesium}octabromide (**1**).

UV–Vis spectra of complex in solvents of different polarity (dichloromethane, ethanol, chloroform and pyridine) are given in (Fig. 3.18). There is almost no difference with respect to the changes in the nature of the solvent. As expected for a porphyrazine core, there are two intense absorptions: one of them in the UV-range around 366 nm and another at the lower energy side of visible region (670 nm). In most tetrapyrrole derivatives, Q band absorption is more intense than B band absorption although both of them correspond to p→p* transition (McKeown, 1998 ; Ahsen, Yılmazer et al., 1988 ; Okur, Gül et al., 1990). When we compare the absorbance values in these two peaks, the one in the UV-range is higher. The reason for this controversy is the combination of p→p* transitions of phenyl groups in triphenylphosphonium units with the B band of the porphyrazine core.

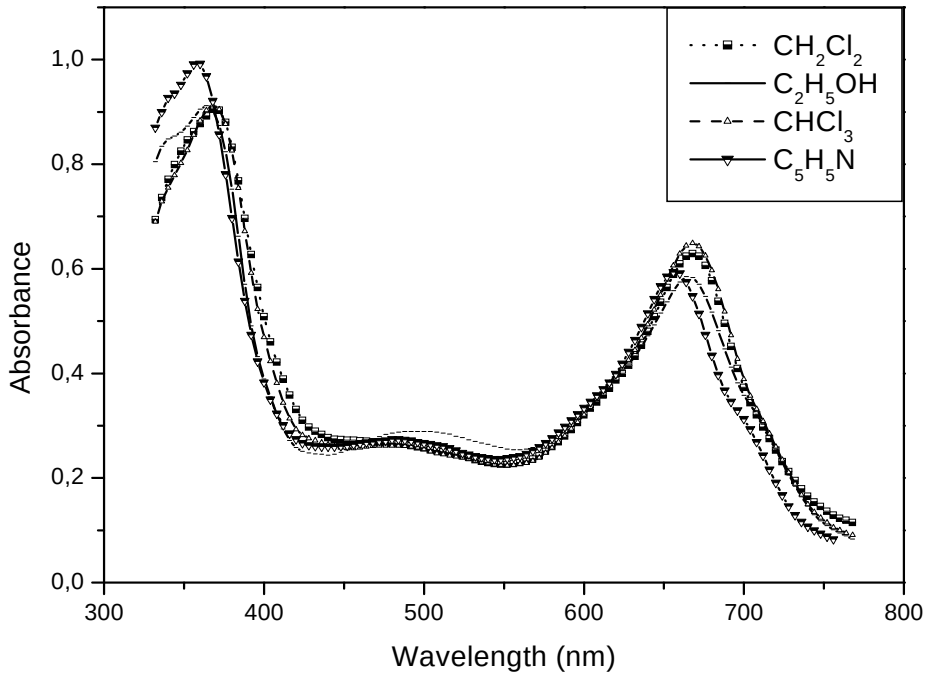


Figure 3.18 UV–Vis spectra of **1** in various solvents.

3.3.7 Phthalocyanine-Porphyrazine Hybrid and its Palladium(II) Complex

A phthalocyanine-porphyrazine hybrid molecule composed of three phthalonitrile units and one maleonitrile moiety was prepared by cyclomerization of the reactants in the presence of magnesium butoxide. Two thioether groups fused to pyrrol positions were complexed with $PdCl_2$ (Fig. 3.19) (Sesalan and Gül, 2000).

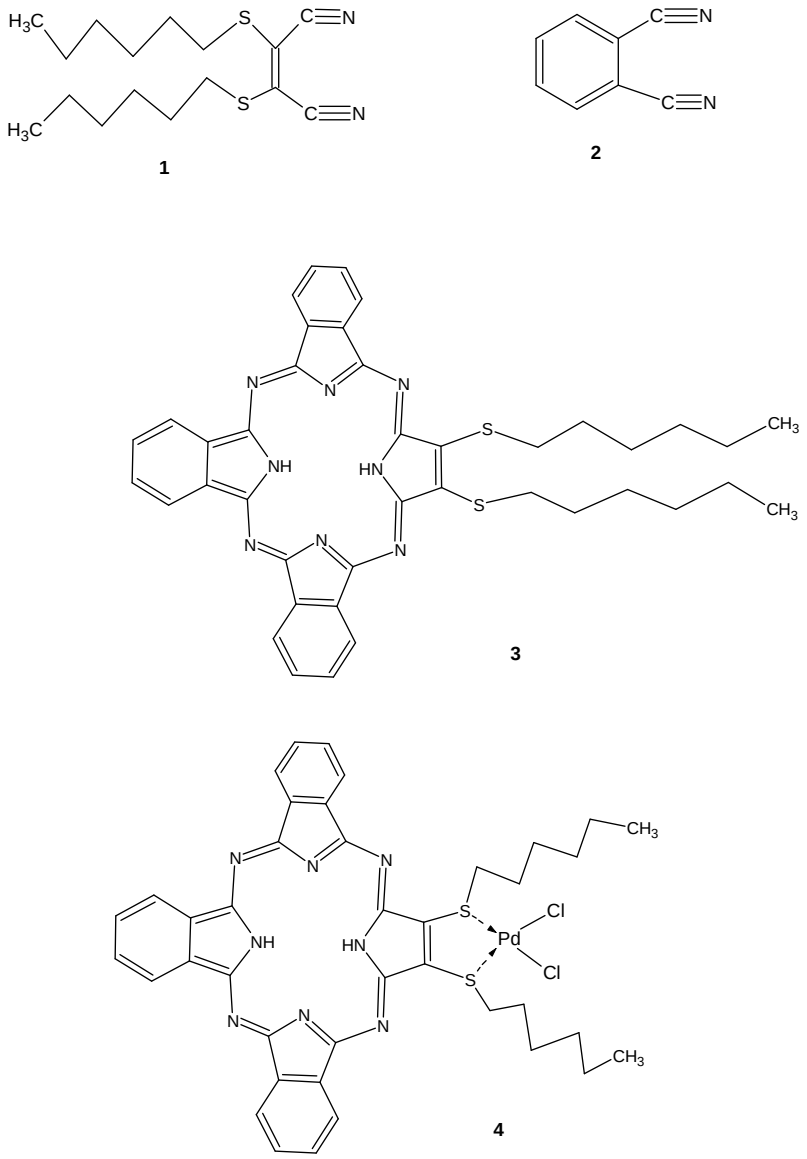
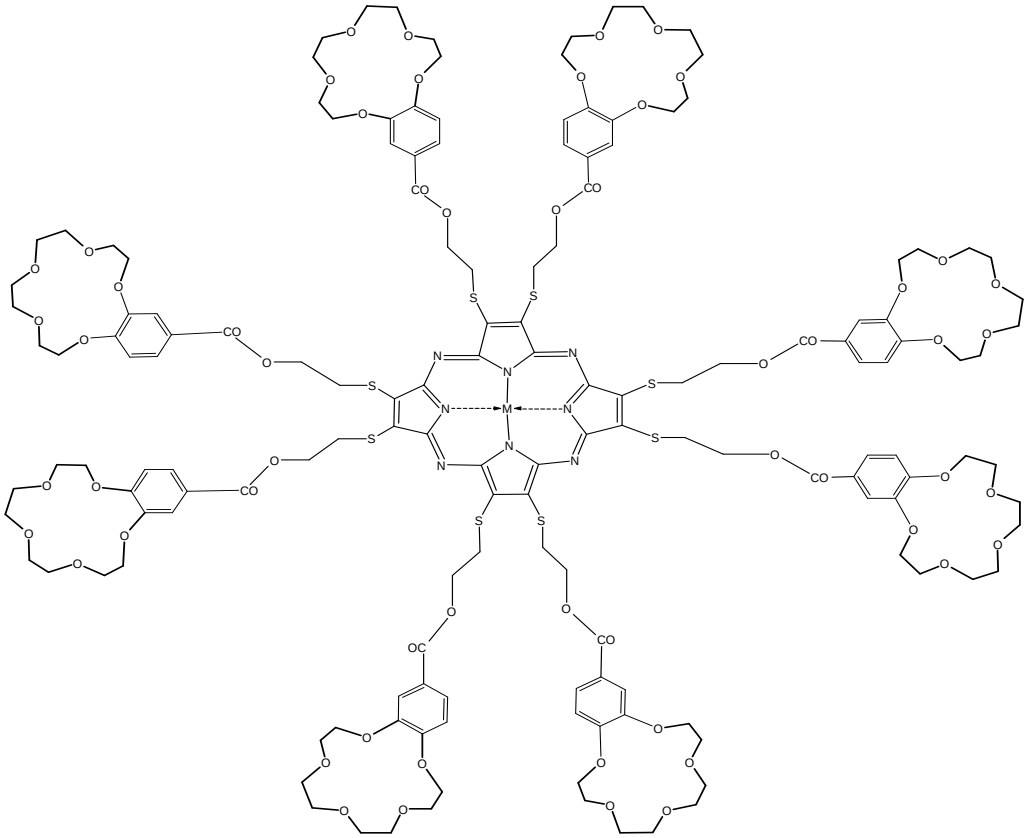


Figure 3.19 Bis-hexylthio-maleonitrile (**1**), phthalonitrile (**2**), phthalocyanine-porphyrazine hybrid (**3**), and the four-coordinate palladium complex (**4**).

3.3.8 Porphyrazines with Appending Eight Crown Ethers

Porphyrazines (M= 2H, Mg, Cu, Co or Zn) with eight crown ether groups appending on the periphery through flexible alkylthio-bridges have been synthesized through esterification of octakis (hydroxyethylthio)-porphyrazinatomagnesium with a carboxylic acid derivative of benzo-15-crown-5 in the presence of dicyclohexyl-

carbodiimid (Fig. 3.20). Alkali metal interaction of the crown ethers on the magnesium porphyrazinate are shown to form intramolecular sandwich type adducts by the changes occurring after gradual portion wise addition of these salts into the porphyrazine solutions (Sağlam and Gül, 2001).



M: **Mg** **2H** **Co** **Cu** **Zn**

4 **5** **6** **7** **8**

Figure 3.20 Octakis (crown ether) substituted phthalocyanines.

3.3.9 Porphyrazines with Bulky Substituents

Magnesium porphyrazinate substituted with eight 4-tert-butylphenylthio-groups on the peripheral positions has been synthesized by cyclotetramerization of 1,2-bis(4-tert-butylphenylthio)maleonitrile in the presence of magnesium butanolate. The metal-free derivative was obtained by its treatment with trifluoroacetic acid and further reaction of this product with copper(II) acetate, zinc(II) acetate and cobalt(II) acetate led to the metal porphyrazinates (M = Cu, Zn, Co) (Fig. 3.21). By using EPR technique, room temperature paramagnetic properties of Cu(II) doped porphyrazine sample as

powder and solution forms were measured. The first-derivative EPR signals taken from as powder and solution forms shows that the sample is axially symmetric. The trend $g_{ll} > g_{\perp} > 2$ indicates that the unpaired electron is located mainly in the d_{x2_y2} orbital ($^2B_1$ as ground state) (Keskin, Köseoğlu et al., 2008).

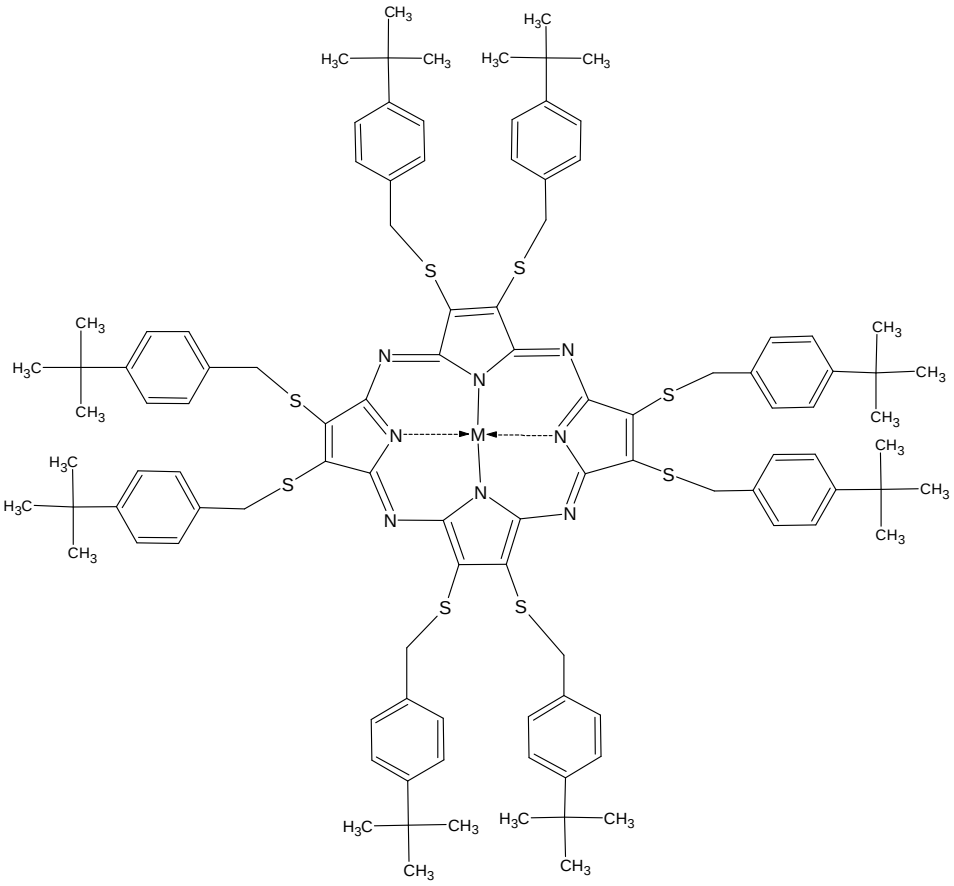


Figure 3.21 Octakis(4-tert-butylbenzylthio) substituted porphyrazines (M =Mg; 2H; Cu; Co; Zn).

3.3.10 Construction of Nonanuclear Supramolecular Structures from Simple Modular Units

A porphyrazine based supramolecule with a nonanuclear structure has been prepared by the ready coordination of pyridine donor sites in octakis(4-pyridoxyethylthio) porphyrazinatomagnesium with vanadyl bis(acetylacetonate) (Fig. 3.22) (Öztürk and Gül, 2004).

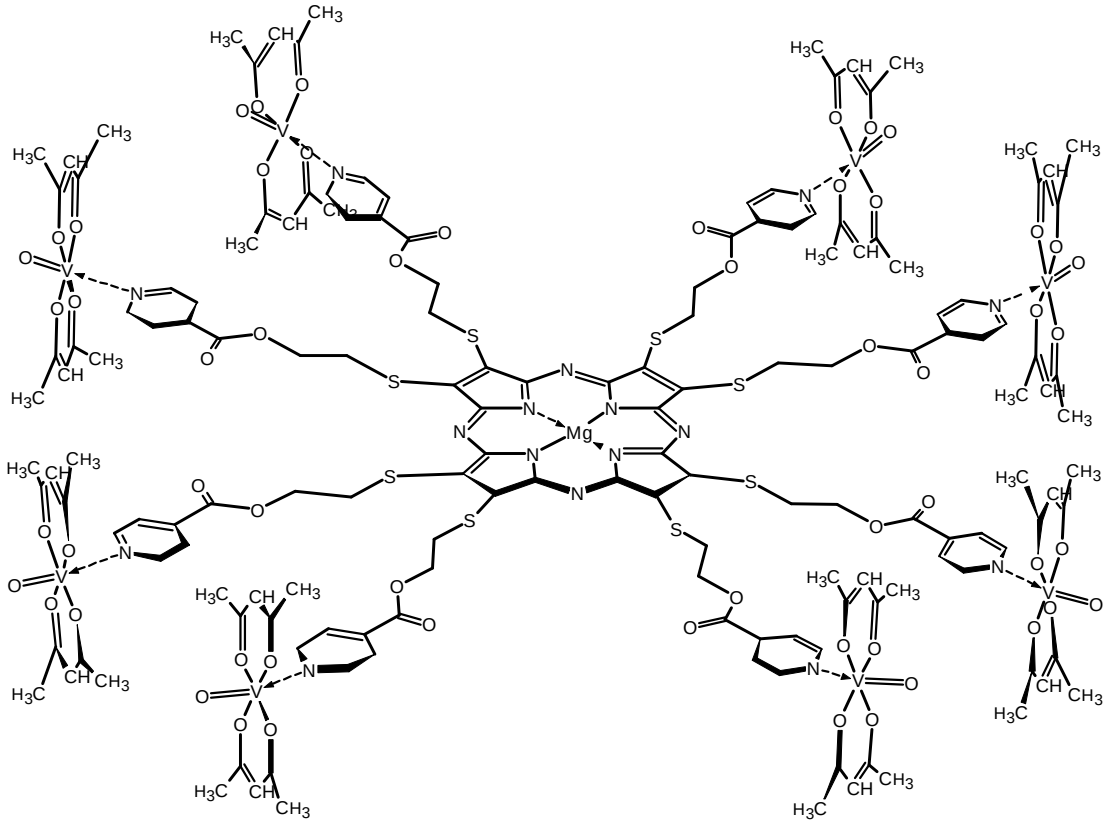


Figure 3.22 Octakis (4-pyridoxyethylthio) porphyrazinatomagnesium with vanadyl bis(acetylacetonate) $[VO(acac)_2(4\text{-}pyCOOCH_2CH_2S)]_8$ MgPz.

3.3.11 Octakis (ferrocene) Substituted Porphyrazines

Metal-free porphyrazine and metal porphyrazinates (M= Mg, Cu, Co or Zn) substituted with eight ferrocene moieties on the periphery through flexible alkylthio-bridges have been synthesised in a multi-step reaction sequence (Fig. 3.23) (Akkuş and Gül, 2001).

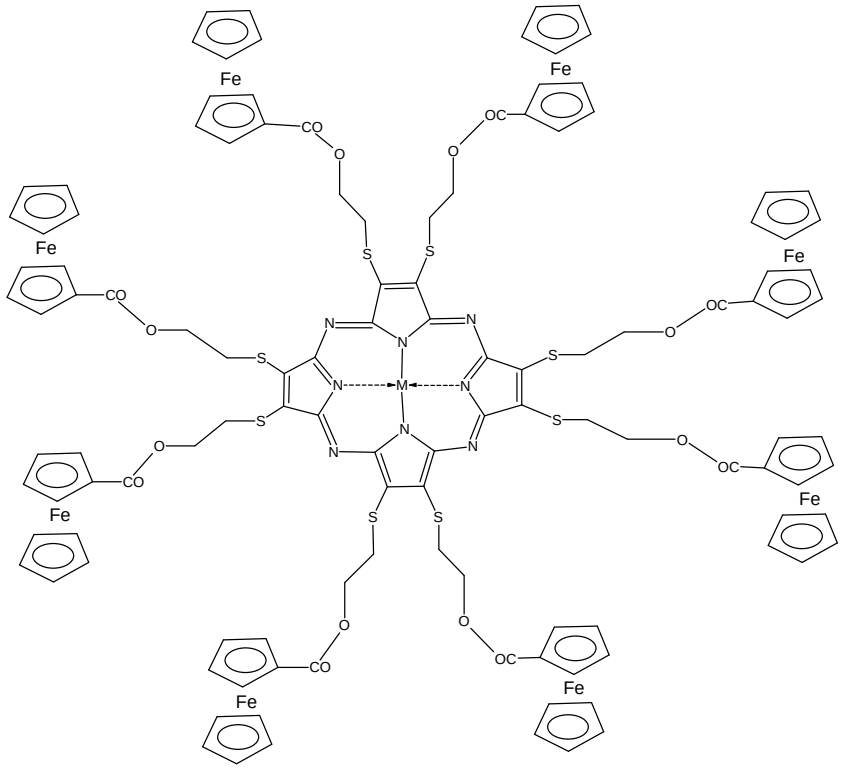
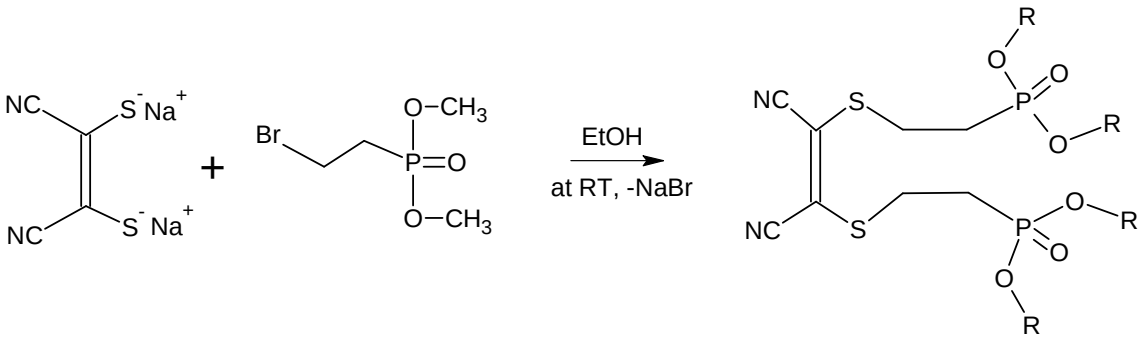


Figure 3.23 Octakis(ferrocene)substituted porphyrazines.

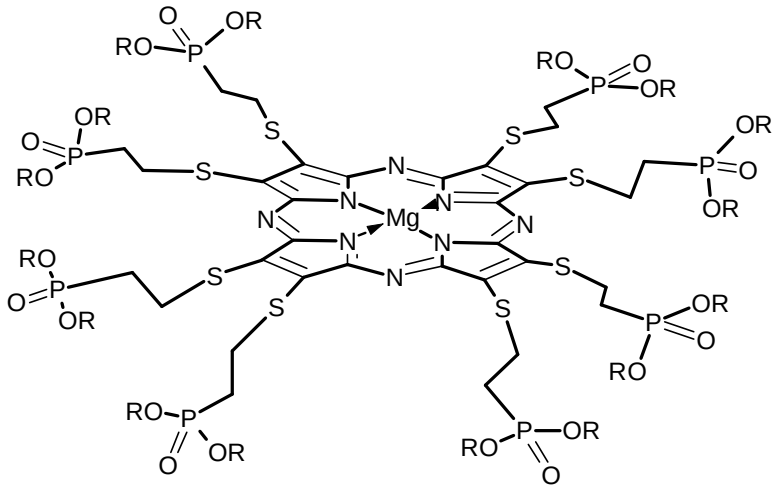
3.3.12 Phosphonic Acid-Substituted Porphyrazines

It is synthesized phosphonate-substituted maleonitrile **1** by the reaction of dithiomaleonitrile disodium salt with diethyl(2-bromoethyl)phosphonate in absolute ethanol under nitrogen at ambient temperature for 12 h (Fig. 3.24). The phosphonate-substituted porphyrazine molecule **2** has been prepared by the Linstead macrocyclization of 1,2-bis{2-(diethylphosphonate) ethylthio}maleonitrile with freshly prepared $Mg(OPr)_2$ in 1-propanol under reflux for 12 h (Fig. 3.25). The proposed structures of maleonitrile **1** and porphyrazine **2** are consistent with their spectral characterizations; the phosphonate groups were easily identified by FT-IR, ^{31}P and ^{13}C NMR spectroscopy. Because of the macrocyclization, the phosphorous peak of the $P{=}O(OR)_2$ groups of maleonitrile shifts from doublet 26.5 to 29.8 ppm in ^{31}P NMR spectrum (Kemikli and Öztürk, 2008).



1

Figure 3.24 Synthesis of 1,2-bis{2-(diethyl phosphonate) ethylthio}maleonitrile **1**.



2

R: Ethyl or Propyl

Figure 3.25 The structure of magnesium octakis(2-(diethylphosphonate)ethylthio) porphyrazine.

3.3.13 Octakis (3-Methylbutylthio) Substituted Porphyrazines

Porphyrazines, MPz (M = Mg, H, Ni, Zn and Co) with octakis (3-methylbutylthio) substituents have been synthesized starting with the corresponding unsaturated dicarbonitrile derivative (Erdoğmuş, Koca et al., 2008).

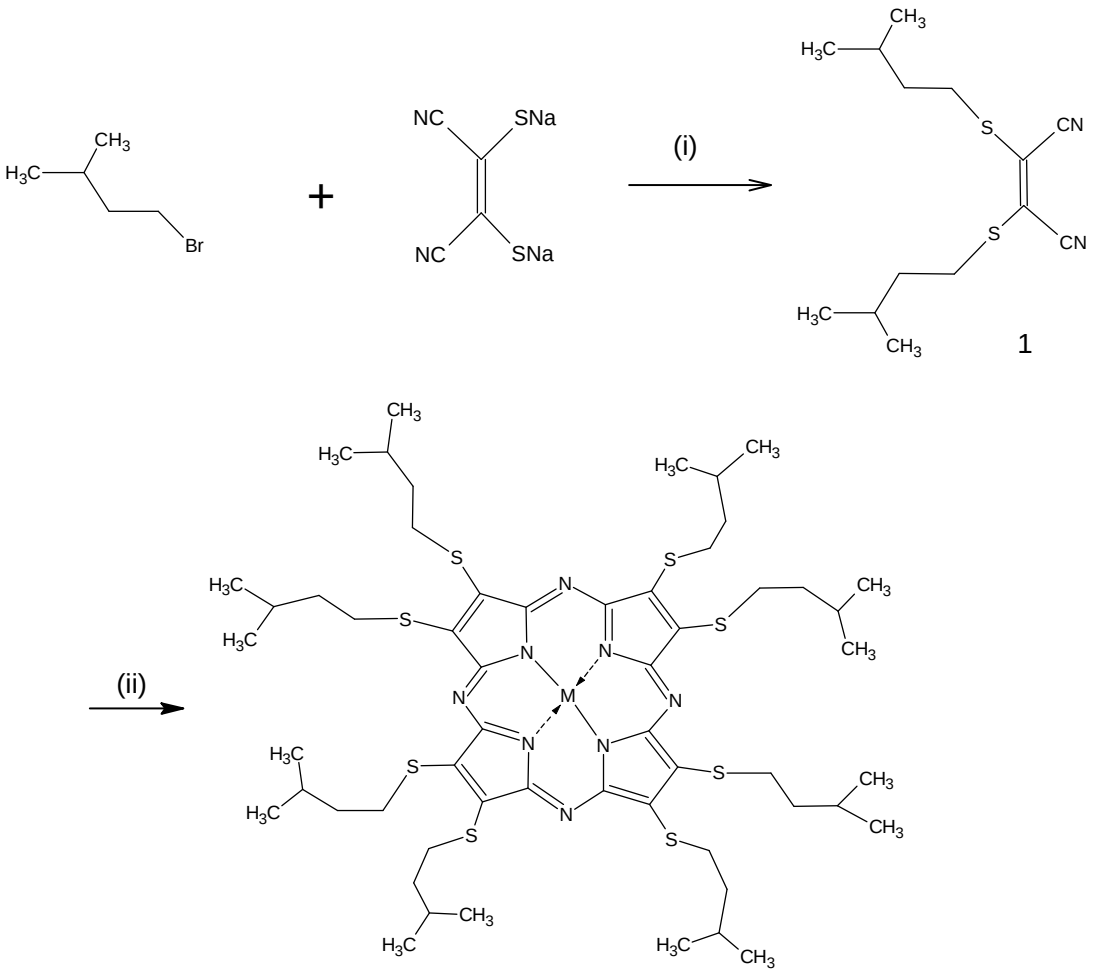


Figure 3.26 (**i**) Acetone, (**ii**) $Mg(BuO)_2$; CF_3COOH; $M(OAc)_2 \cdot 4H_2O$ (M: Ni, Zn,Co). Bis(3-methylbutylthio) maleonitrile (**1**) and the porphyrazines (**2-6**) derived from it.

The electronic absorption spectra of the metal-free porphyrazine **3** exhibited a splitted Q band absorption which is due to $\pi \longrightarrow \pi^*$ transitions of these completely conjugated 18 π electron systems. With the insertion of metal into the core of porphyrazines, the characteristic Q band transitions of the metal porphyrazinates were observed as a single band of high intensity. The effect of eight S-substituents on the periphery of the porphyrazine core was a shift in these intense Q bands to longer wavelengths when compared with those of unsubstituted or alkyl substituted derivatives (Kobayashi, Leznoff et al., 1993). The Q and B bands absorptions and logarithmic coefficient values for **4**, **5** and **6** are at 666 nm (4.89), 326 nm (4.62); 673 nm (4.90),

374 nm (4.65) and 674 nm (4.85), 376 (4.56) respectively. The UV spectra of the compounds **2**, **3**, **4**, **5** and **6** are given in the Figure 3.27.

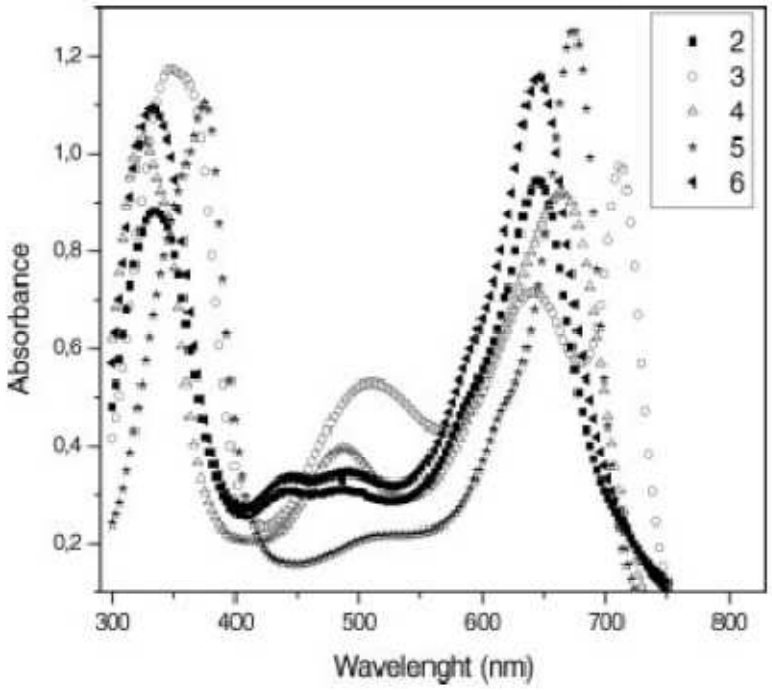


Figure 3.27 UV spectra of **2**, **3**, **4**, **5** and **6** in chloroform.

3.3.14 Metal-Linked Trinuclear Porphyrazine Dimer

This report presents the synthesis and characterization of a soluble porphyrazinedithiolate ligand and its metal complexes. As a first step toward the assembly of metal-linked multiporphyrazine arrays, we have linked two of the porphyrazinedithiolates by a metal ion (Ni(III)) to form a novel trimetallic metal-linked porphyrazine dimer (Baumann, Barrett et al., 1997).

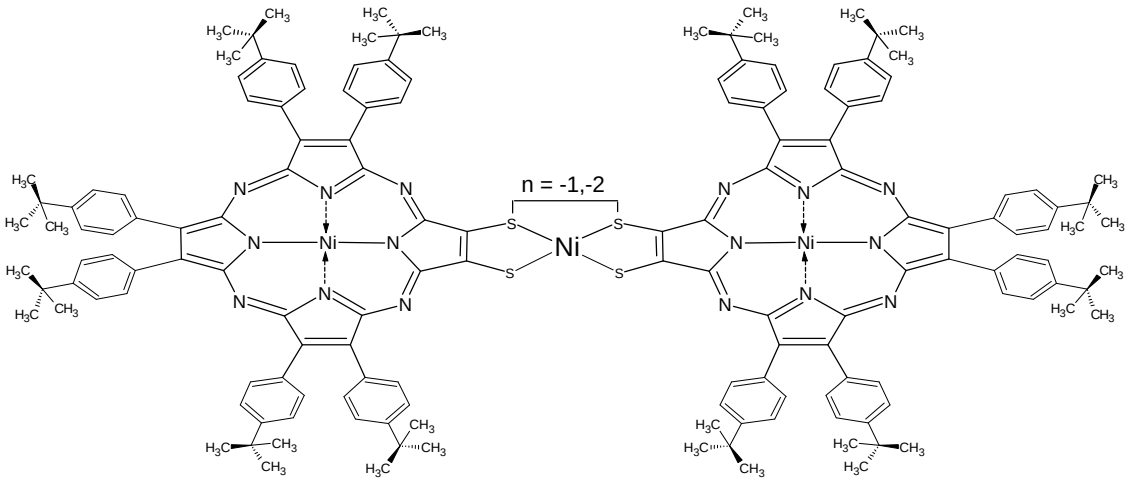


Figure 3.28 Trimetallic metal-linked porphyrazine dimer.

3.3.15 Dithiacrown Ether Substituted Porphyrazines

In this work gives a full account of the synthesis and physical properties of porphyrazines to which four sulfur-containing crown ether rings of various sizes are connected: dithia-7-crown-2 (**b**), dithia-15-crown-5 (**c**), and dithia-18-crown-6 (**d**). The presence of the sulfur atoms in the crown ether rings gives the opportunity to bind soft transition-metal ions. Thiacrown ethers **2**(*n*) (*n* = 1-2) containing 1,2-dicyano-1,2-dithioethene were used as the precursors for the crowned porphyrazines (van Nostrum, Benneker et al., 1996).

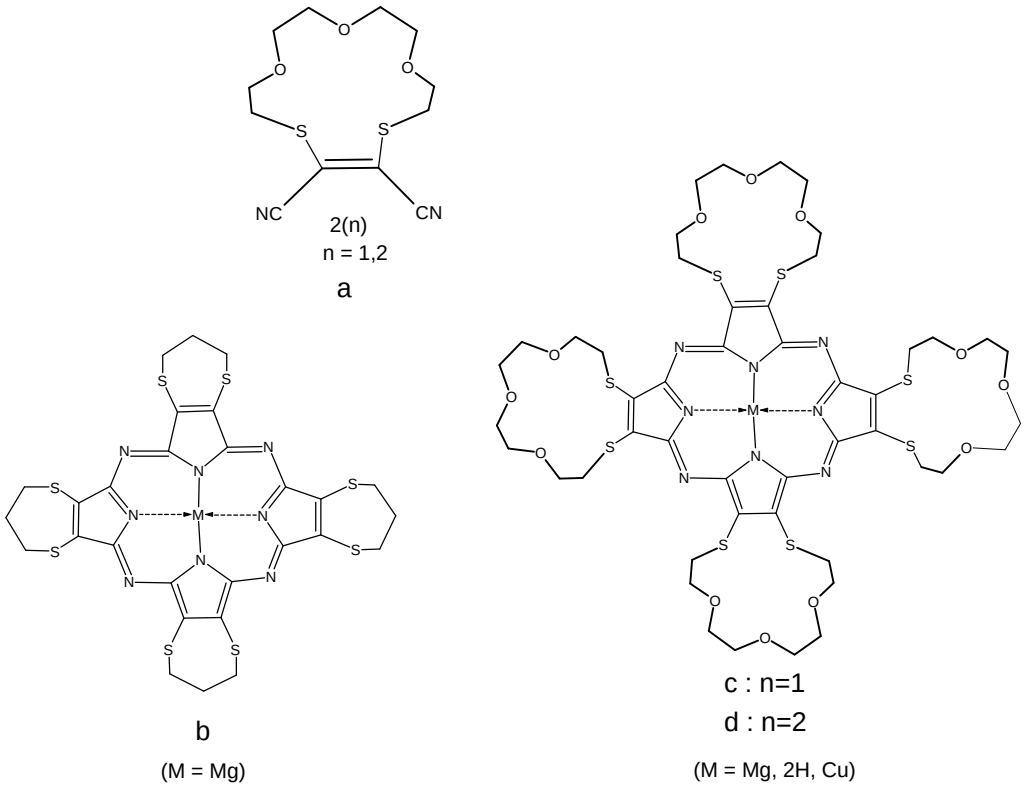


Figure 3.29 (**a**) (2(1)) : 1,2-Dicyano-3,15-dithia-6,9,12-trioxacyclopentadecene
(**b**) {Tetrakis([1,5]dithiacyclohepteno)[6,7-*b*:6′,7′-*g*:6″,7″-*l*:6‴,7‴-*q*]-porphyrazinato}magnesium(II)
(**c**) {Tetrakis([1,4,7,10,13]trioxadithiacyclopentadeceno)[11,12-*b*:11′,-12′-*g*:11″,12″-*l*:11‴,12‴-*q*]porphyrazinato}magnesium(II)
(**d**) {Tetrakis([1,4,7,10,13,16]tetraoxadithiacyclooctadeceno)[14,15-*b*:14′,15′-*g*:14″,15″-*l*:14‴,15‴-*q*]porphyrazinato}magnesium(II)

3.3.16 Quarternized porphyrazine ion in aqueous solution

In that study, a water-soluble quaternized cobalt porphyrazine was synthesized and used as buffer additive to separate the positional isomers of naphthalenesulfonates and chlorobenzoates employing ion-exchange electrokinetic chromatography (Kavran, Akkuş et al., 2002). The structure of [octakis(2-trimethylammoniumethylthio) porphyrazinatocobalt]-octaiodide (CoPzq) is given in Figure 3.30. The structures of the analytes are given in Figure 3.31.

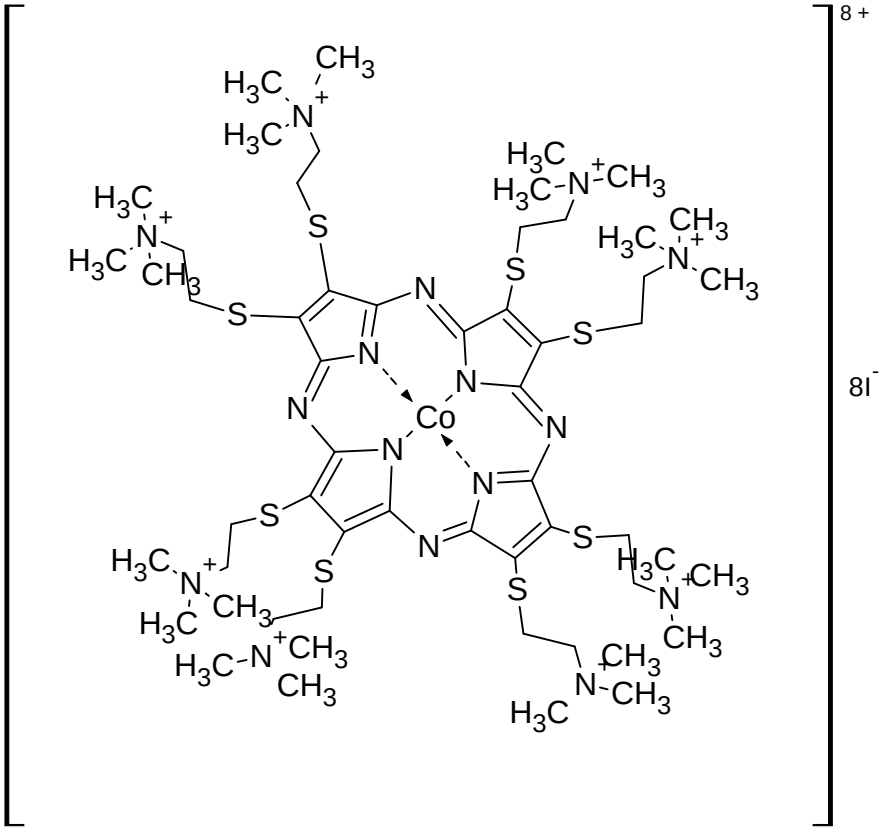
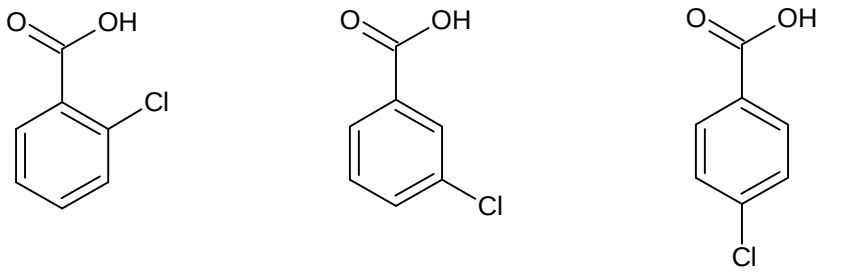


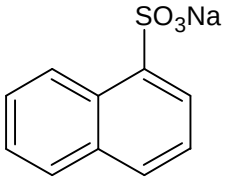
Figure 3.30 Structure of [octakis(2-trimethylammoniumethylthio)porphyrazinatocobalt] octaiodide (CoPzq).



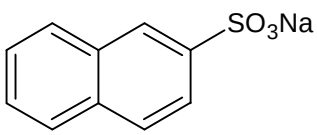
2-Chlorobenzoic acid

3-Chlorobenzoic acid

4-Chlorobenzoic acid



Naphthalene-1-sulfonic acid



Naphthalene-2-sulfonic acid

Figure 3.31 The structures of the analytes.

3.3.17 Phthalocyanines containing macrocycle units

A soluble metal-free phthalocyanine **5** and its metal complexes (Zn, Ni, Co and Cu) **6, 7**, **8** and **9** containing eight 16-membered tetrathiamonoaza macrocycles on peripheral substituent positions have been synthesized. The metal-free phthalocyanine **5** was synthesized from 4,5-bis{[2-(1,4,10,13-tetrathia-7-azacyclohexadecan-7-yl) ethyl]oxy}phthalonitrile **4**. The metal complexes **6, 7** and **8** were prepared by a tetramerization reaction of the phthalonitrile derivative 4 with appropriate materials (Fig. 3.32). Copper(II) phthalocyanine **9** was prepared by the reaction of 4,5-bis{[2-(1,4,10,13-tetrathia-7-azacyclohexadecan-7-yl)ethyl]oxy}-1,2 dibromobenzene **3** with excess CuCN and dry quinoline (Fig. 3.33). Liquid–liquid extraction of several heavy metal ions such as Ag^{+}, Hg^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} with compound **5** was also tested using picrate as the anion of the ion pair. The extraction avidity of **5** for Ag^{+} was found to be highest in the liquid–liquid phase extraction experiments (Ertem, Bilgin et al., 2008).

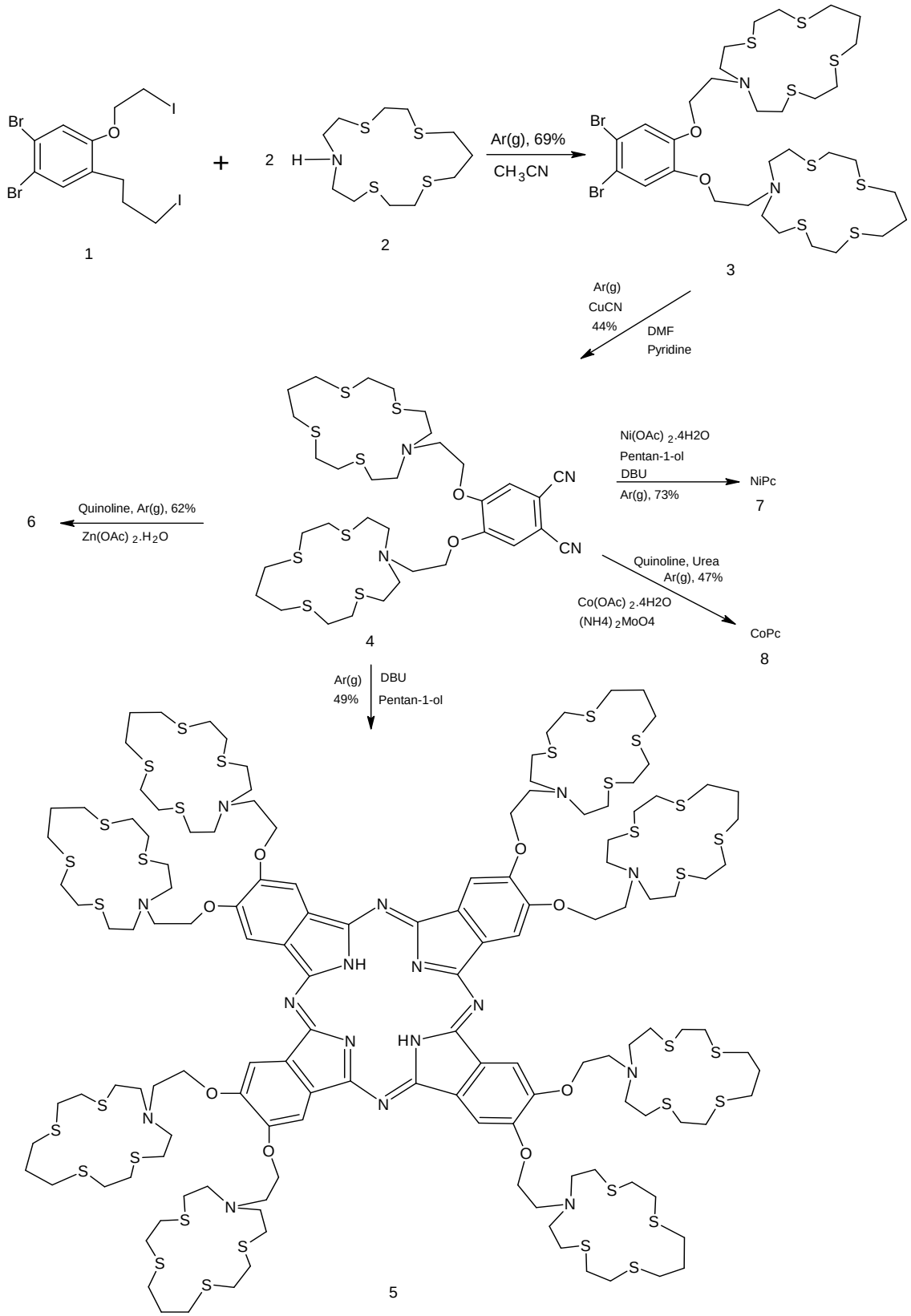


Figure 3.32 Synthesis of metal-free and metallo (Zn, Ni, Co) phythalocyanines.

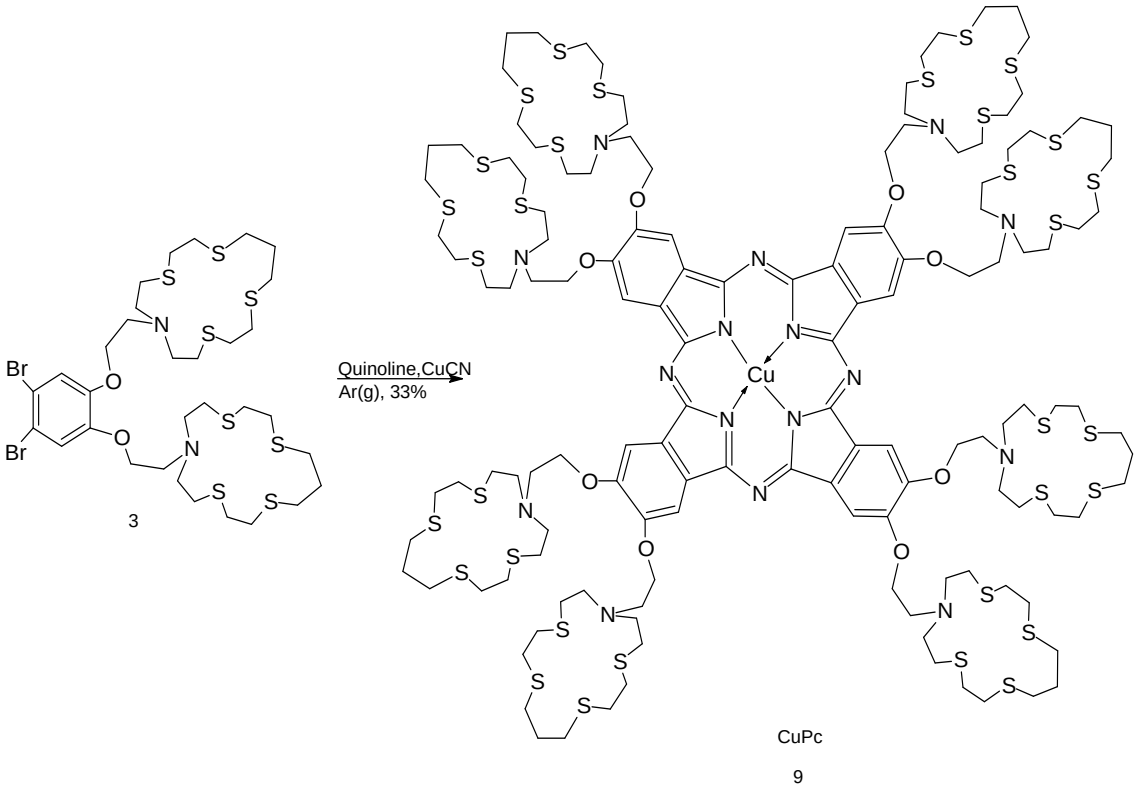


Figure 3.33 Synthesis of copper phythalocyanine.

3.3.18 Porphyrazines with Tertiary or Quaternized Aminoethyl Substituents

Metal-free and metallo porphyrazines (M=Mg or Co) carrying eight dimethylaminoethylthia-groups on peripheral positions have been synthesized from the disodium salt of dithiomaleonitrile and the hydrochloride of dimethyl-aminoethylchloride (Polat and Gül, 2000). The magnesium derivative (MgPza) was converted into quaternized product (MgPzq) (Fig. 3.34) by reaction with methyl iodide. The metal-free derivative was obtained by treatment with trifluoroacetic acid and its reaction with cobalt (II) acetate led to the cobalt derivative (CoPza). Aggregation of MgPzq molecules (Fig. 3.35) has been observed in aqueous solution by the blue-shift of the Q-band absorption with an accompanying decrease in intensity.

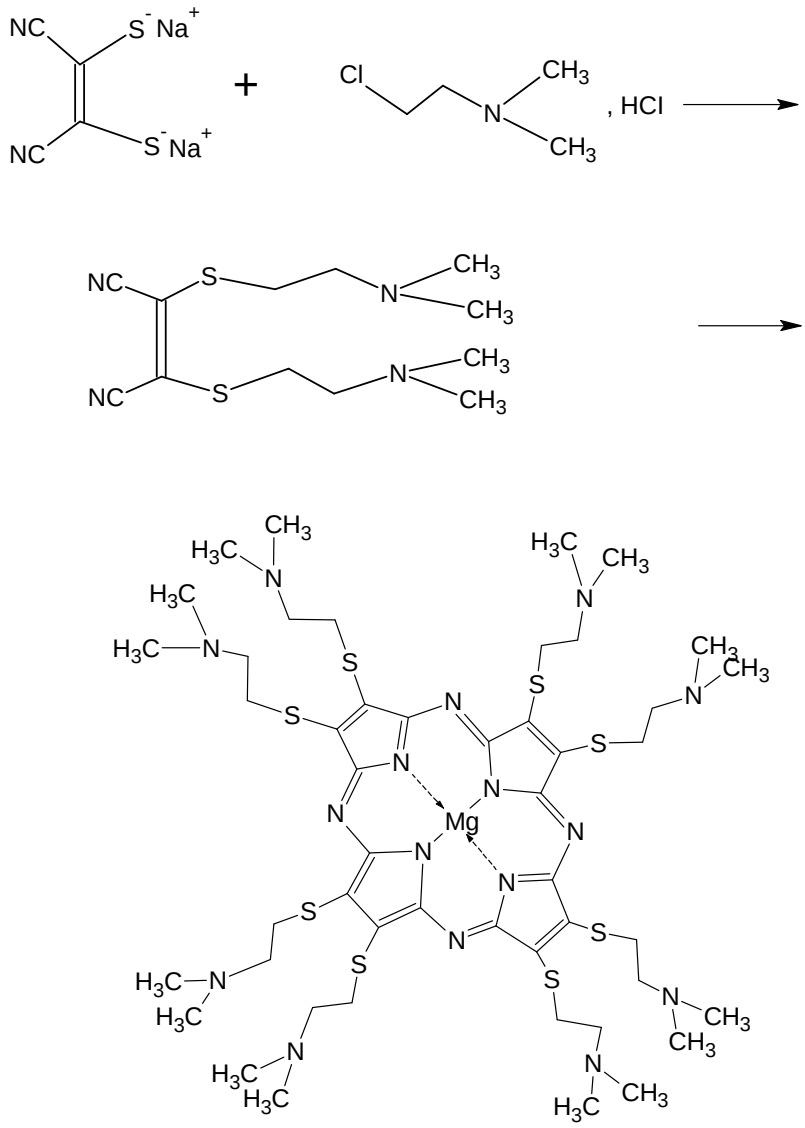


Figure 3.34 Octakis(2-dimethylaminoethylthio) porphyrazinato-magnezyum (MgPza).

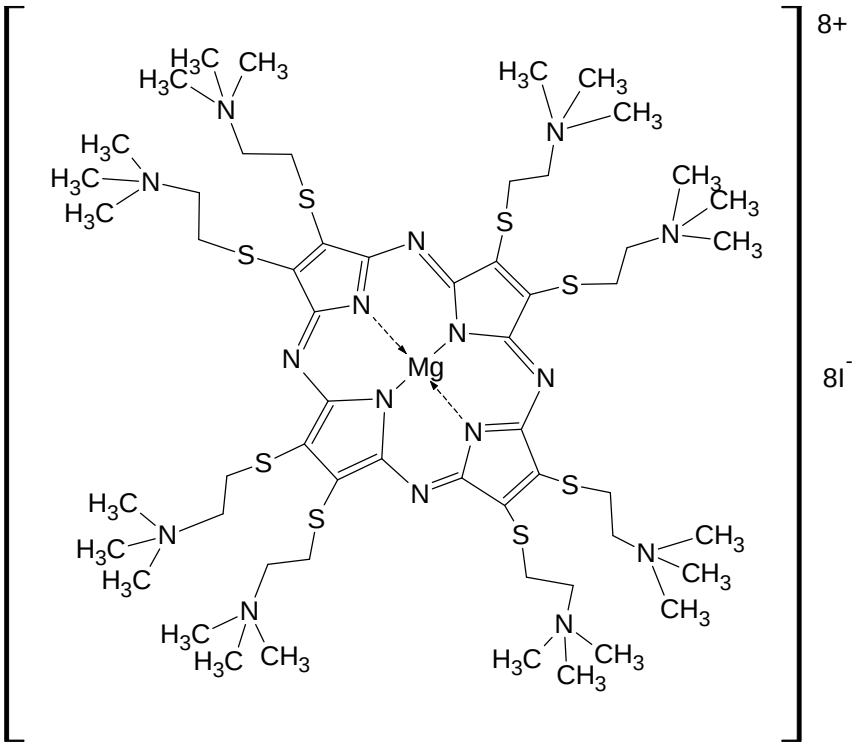


Figure 3.35 [Octakis (2-trimethylammoniumethylthio) porphyrazinato-magnesium] octaiodide (MgPzq).

3.3.19 Octakis(Octylthio)Porphyrazinato-iron Derivatives

Chlorooctakis (octylthio)porphyrazinatoiron(III) (FePzCl) was prepared by the reaction of metal-free porphyrazine with iron(II) acetate and further treatment with HCl solution (Fig. 3.36). The monomeric bisaxial complex $FePz(py)_2$ (Fig. 3.37) as well as the bridged complex [FePz(pyz)]n (Fig. 3.38) were formed as stable complexes by reacting FePzCl with pyridine or pyrazine, respectively. These complexes were characterized by elemental analysis and spectroscopic methods (Hasanov and Gül, 2001).

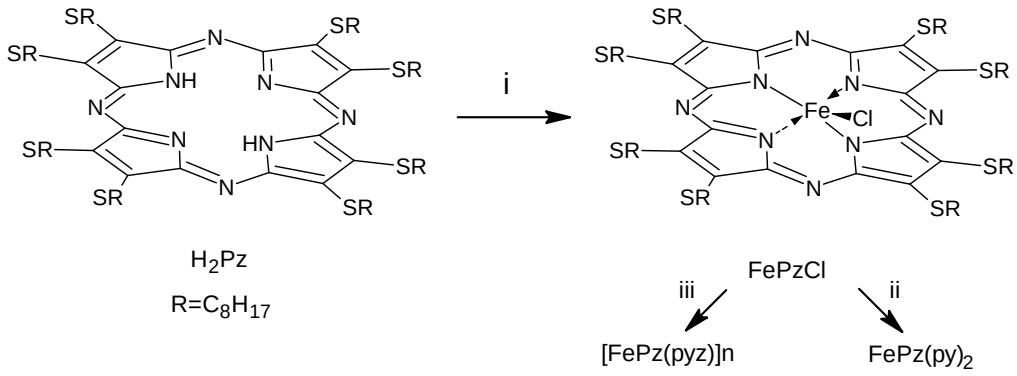


Figure 3.36 Synthesis route to new compounds: (**i**) $Fe(OAc)_2$, acetic acid, HCl; (**ii**) pyridine; (**iii**) pyrazine.

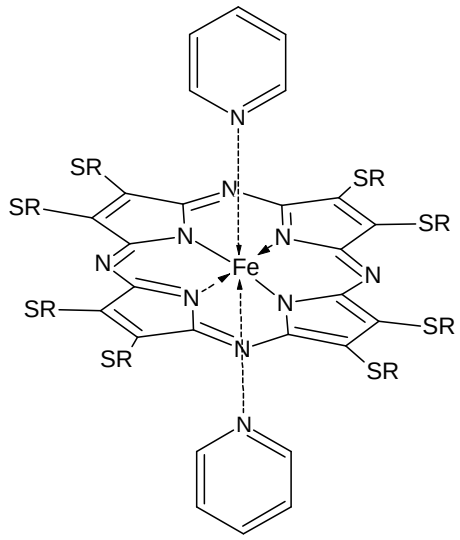


Figure 3.37 $FePz(py)_2$.

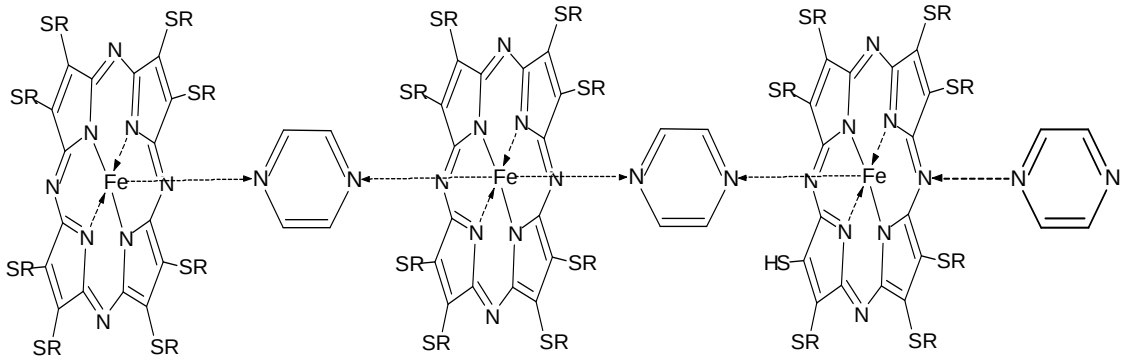


Figure 3.38 $[FePz(pyz)]_n$.

3.4 *Seco*-type Porphyrazines That Bearing Different Substituents

Novel *seco*-porphyrazines substituted with (1-naphthyl), (4-tert-butylphenyl), (*p*-tolyl) and (*o*-tolyl) have been described in this section. These novel compounds have been characterized by elemental analysis, together with FT-IR, ^{1}H NMR, UV-Vis and mass spectral data.

3.4.1 *Seco*-porphyrazines with eight 4-biphenyl groups

Magnesium porphyrazinate substituted with eight 4-biphenyl groups on the periphery positions has been synthesized for the first time from cyclotetramerization of 1,2-bis(4-biphenyl)maleonitrile in the presence of magnesium butanolate. Its demetalation by treatment with trifluoroacetic acid, resulted in a partially oxidized product, namely, octakis(4-biphenyl)-2-*seco*-porphyrazine-2,3-dione. Further reaction of this product with copper(II) acetate, zinc(II) acetate and cobalt(II) acetate has led to the metallo derivatives, [octakis(4-biphenyl)-2-*seco*-2,3-dioxoporphyrazinato] M(II) (M= Cu, Zn, Co) (Fig. 3.39). These novel compounds have been characterized by elemental analysis, together with FT-IR, ^{1}H NMR, UV-Vis and mass spectral data (Gonca, Baklacı et al., 2008).

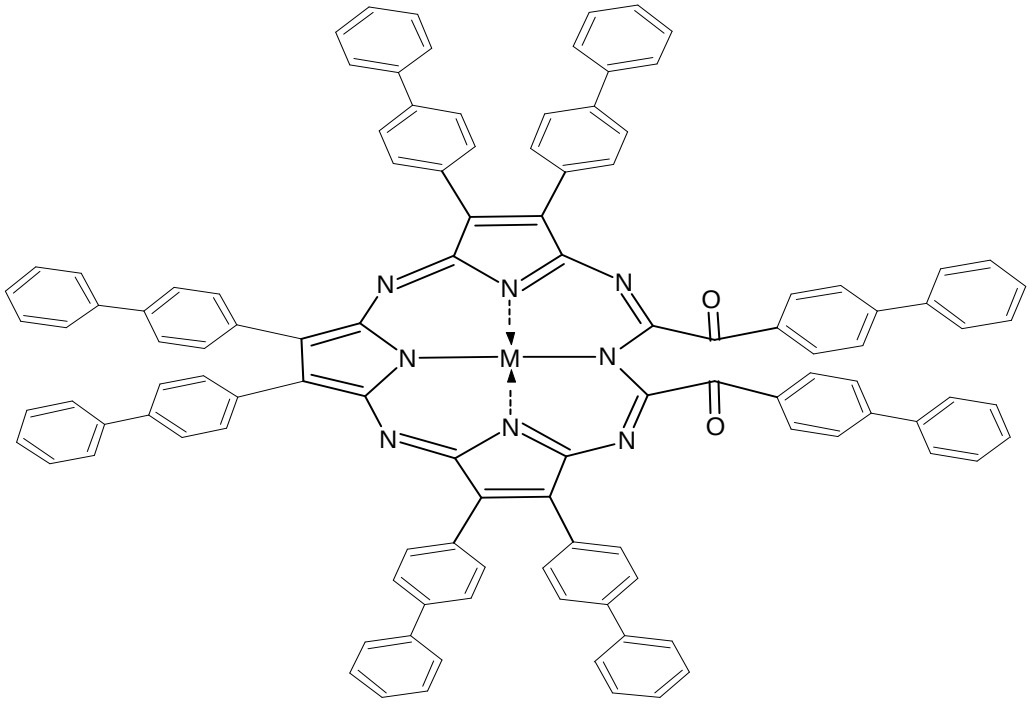


Figure 3.39 Synthesis of [2,3,7,8,12,13,17,18-octakis(4-biphenyl)-2-*seco*-2,3-dioxoporphyrazinato] {M= Cu(II), Zn(II) or Co(II)}.

3.4.2 Soluble *Seco*-Porphyrazines with Bulky Substituents

By cyclotetramerization of 3,4-bis(4-tert-butylphenyl)pyrroline-2,5-diimine in the presence of magnesium butanolate, magnesium porphyrazinate with eight (4-tert-butylphenyl) units on the periphery has been synthesized. Its demetallation by the treatment with trifluoroacetic acid resulted in a partially oxidized product, namely, octakis(4-tert-butylphenyl)-2-*seco*-porphyrazine-2,3-dione. Further reaction of this product with copper(II) acetate, zinc(II) acetate, and cobalt(II) acetate led to the metallo derivatives, [octakis(4-tert-butylphenyl)-2-*seco*-2,3-dioxoporphyrazinato] M(II) (M= Cu, Zn, Co) (Fig. 3.40). These soluble complexes have been characterized by elemental analysis, FT-IR, ^{1}H NMR, UV-Vis, and mass spectral data (Gonca and Keskin, 2009).

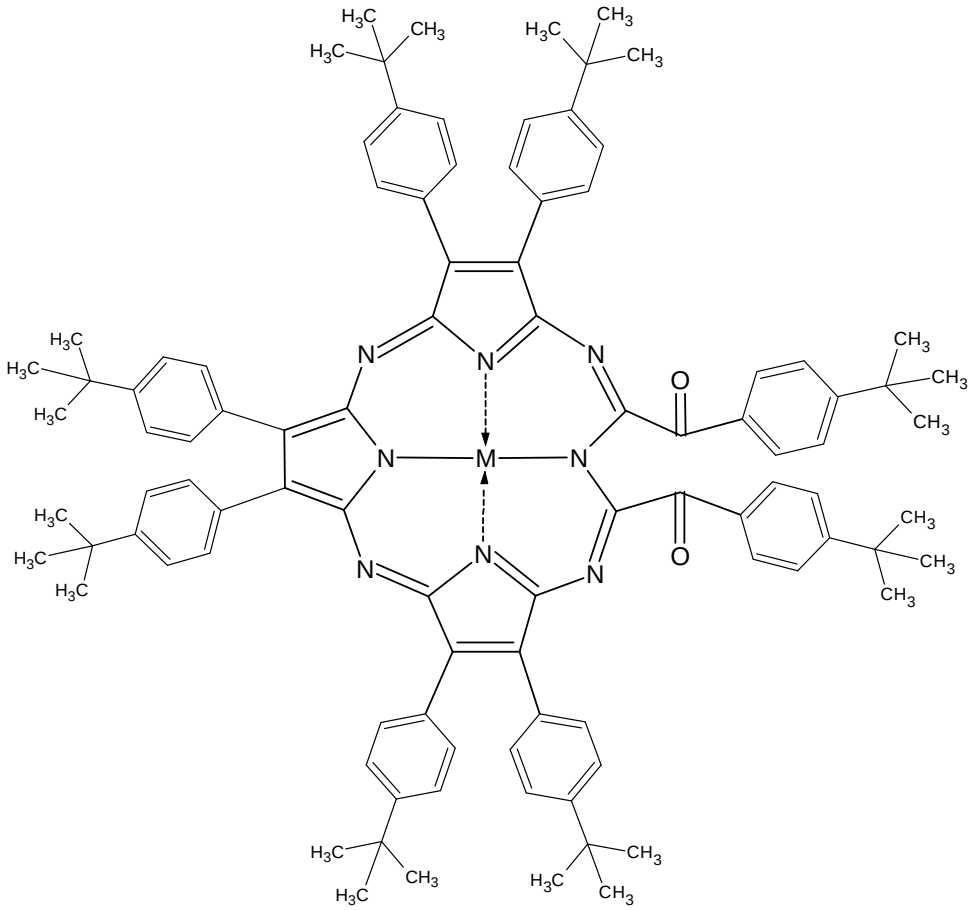
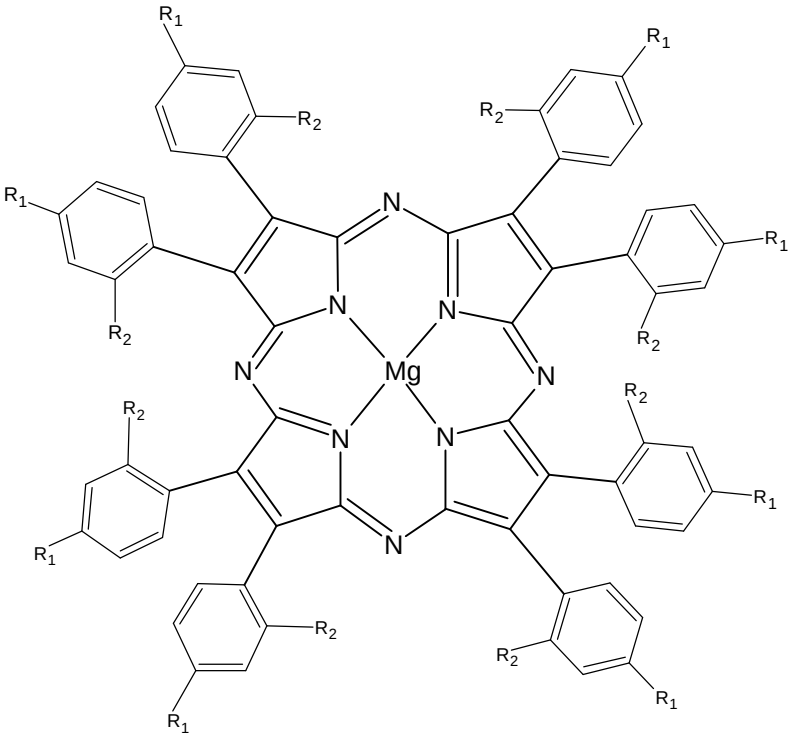


Figure 3.40 [2,3,7,8,12,13,17,18-octakis(4-*tert*-butylphenyl)-2-*seco*-porphyrazine-2,3-dione] and metal derivatives {M= 2H, Cu(II), Zn(II) or Co(II)}.

3.4.3 *Seco*-Porphyrazines with Eight (*p*-tolyl) and (*o*-tolyl) Units

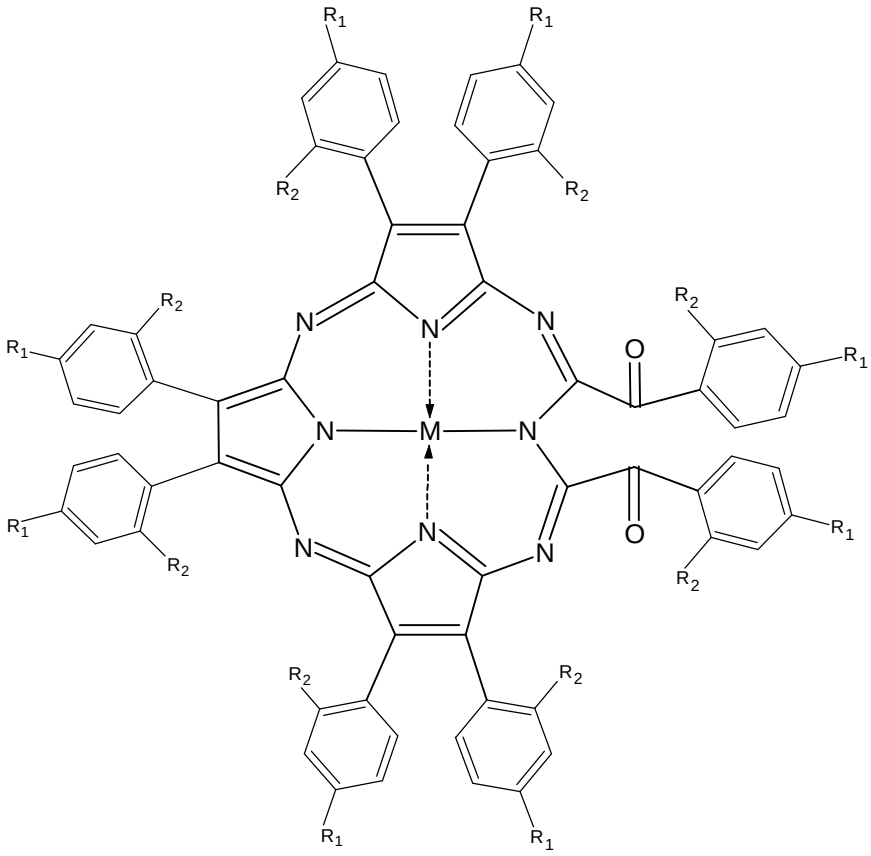
Magnesium porphyrazinates substituted with eight (*p*-tolyl) and (*o*-tolyl) units on the peripheral positions have been synthesized by cyclotetramerization of 1,2-bis(*p*-tolyl)maleonitrile and 1,2-bis(*o*-tolyl)maleonitrile in the presence of magnesium butanolate (Fig. 3.41). Their demetallation by the treatment with trifluoroacetic acid resulted in partially oxidized products, namely, octakis(*p*-tolyl)-2-*seco*-porphyrazine-2,3-dione and octakis(*o*-tolyl)-2-*seco*-porphyrazine-2,3-dione. Further reactions of these products with copper(II) acetate, zinc(II) acetate and cobalt(II) acetate have led to the metallo derivatives, [octakis(*p*-tolyl)-2-*seco*-2,3-dioxoporphyrazinato] M(II) and [octakis(*o*-tolyl)-2-*seco*-2,3-dioxoporphyrazinato] M(II) (M = Cu, Zn, Co) (Fig. 3.42) (Gonca, Baklacı et al., 2008).



1a (R_1: CH_3, R_2: H)

2a (R_1: H, R_2: CH_3)

Figure 3.41 [2,3,7,8,12,13,17,18-octakis(*p*-tolyl)porfirazinato] Mg(II) (**1a**) and [2,3,7,8,12,13,17,18-octakis(*o*-tolyl)porfirazinato] Mg(II) (**2a**).



M= 2H (**1b**); Cu (**1c**); Zn (**1d**); Co (**1e**) (R_1: CH_3, R_2: H)

M= 2H (**2b**); Cu (**2c**); Zn (**2d**); Co (**2e**) (R_1: H, R_2: CH_3)

Figure 3.42 [2,3,7,8,12,13,17,18-octakis(*p*-tolyl)-2-*seco*-porphyrazine-2,3-dione] and metal derivatives {M= 2H, Cu(II), Zn(II) or Co(II)} and [2,3,7,8,12,13,17,18-octakis (*o*-tolyl)-2-*seco*-porphyrazine-2,3-dione] and metal derivatives {M= 2H, Cu(II), Zn(II) or Co(II)}.

3.4.4 Partially Oxidized Porphyrazines

The scope of the present work was to prepare metalloporphyrazinates substituted directly with eight (1-naphthyl) groups on the peripheral positions (Nazlı, Gonca et al., 2006). Magnesium porphyrazinate substituted with eight (1-naphthyl) groups on the peripheral positions has been synthesized by cyclotetramerization of 3,4-(1-naphthyl)pyrroline-2,5-diimine, 4-(1-naphthyl)pyrroline-2,5-diimine in the presence of magnesium butanolate. Its demetalation by treatment with trifluoroacetic acid, resulted in a partially oxidized product, namely, octakis(1-naphthyl)-2-*seco*-porphyrazine-2,3-

dione (Fig.3.43). Further reaction of this product with copper(II) acetate, zinc(II) acetate and cobalt(II) acetate led to the metallo derivatives, [octakis(1-naphthyl)-2-*seco*-2,3-dioxoporphyrazinato]M(II) (M = Cu, Zn or Co).

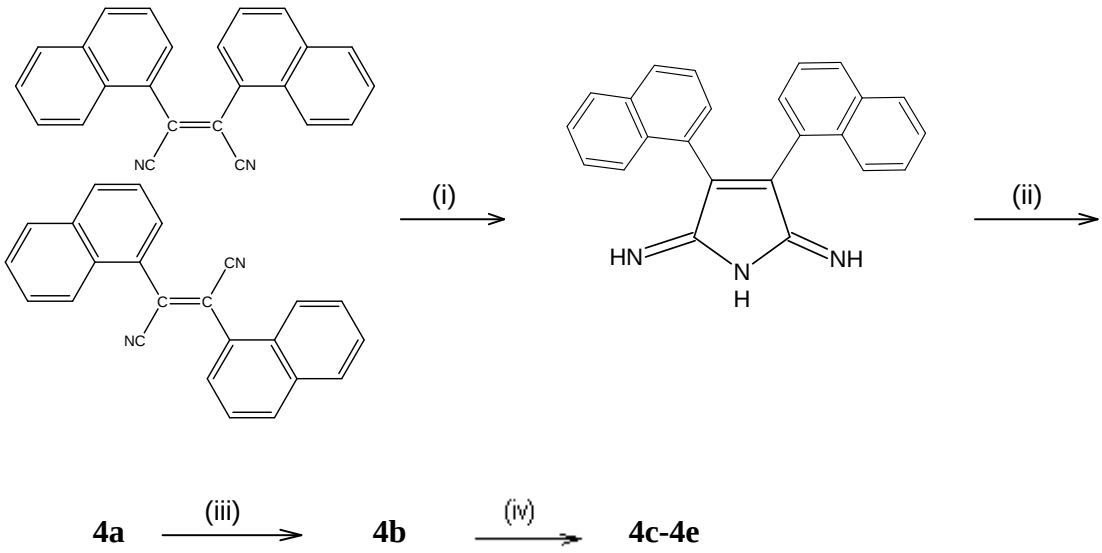
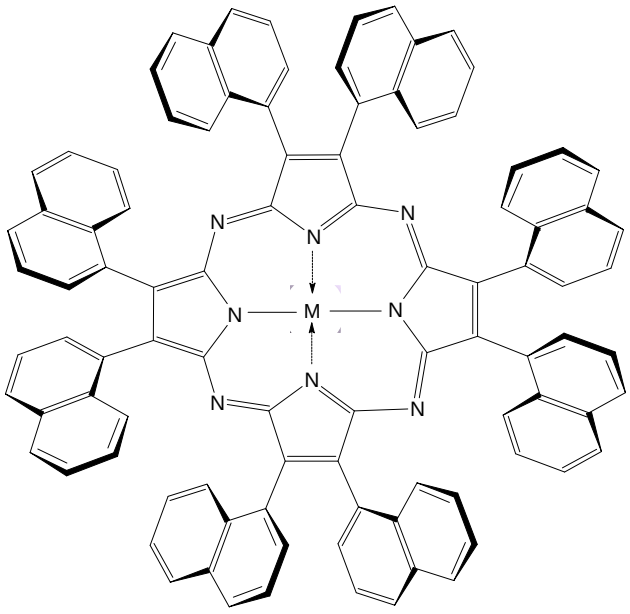
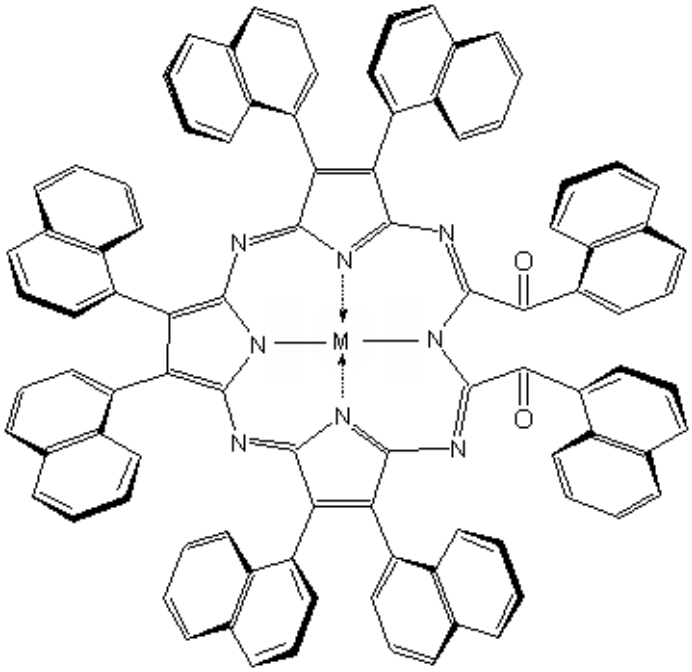


Figure 3.43 (**i**) Ethylene glycol; (**ii**) Mg turnings, I_2, *n*-BuOH; (**iii**) CF_3CO_2H; (**iv**) $CHCl_3$, EtOH and $Cu(OAc)_2$, $Zn(OAc)_2$, or $Co(OAc)_2$.



M = Mg (**4a**)

Figure 3.44 [2,3,7,8,12,13,17,18-Octakis(1-naphthyl) porphyrazinato] Mg(II).



M = 2H (**4b**); Cu (**4c**); Zn (**4d**); Co (**4e**)

Figure 3.45 [2,3,7,8,12,13,17,18-octakis(1-naphthyl)-2-*seco*-porphyrazine-2,3-dione] and metal derivatives [M = 2H, Cu(II), Zn(II) or Co(II)].

3.5 The Aim and Scope of This Work

The synthesis of novel porphyrazines with eight (2-anthraquinonylmethylthio) substituent derivative will be the main scope of this work. Magnesium porphyrazinates will be synthesized by cyclotetramerization of 2,3-bis(2-anthraquinonylmethylthio) maleonitrile in the presence of magnesium butanolate. The conversions of magnesium porphyrazinates into the metal-free derivatives will be achieved by the treatment with relatively strong acids (e.g. trifluoroacetic acid). Further reactions of this product with copper(II) acetate, zinc(II) acetate and cobalt(II) acetate will be led to the metal porphyrazinates ($M^{2+} = Cu^{2+}$, Zn^{2+}, Co^{2+}).

The synthesis along with the spectroscopic properties of the novel compounds will be described.

CHAPTER 4

CHEMICALS AND EQUIPMENT

4.1. Chemicals

2-(chloromethyl)anthraquinone, Sodium Cyanide (NaCN), Dimethylformamide (DMF), Carbon Disulfide (CS_2), Isobutanol, Methanol (CH_3OH), Ethanol (C_2H_5OH), Iodine (I_2), Magnesium (Mg), Sodium Sulfate (Na_2SO_4), Chloroform ($CHCl_3$), Dichloromethane (CH_2Cl_2), Ammonia (NH_3), Trifluoroacetic acid (CF_3COOH), *n*-Butanol (C_4H_9OH), Diethylether ($C_4H_{10}O$), Benzene (C_6H_6), Acetone (C_3H_6O), Paraffin Oil, *n*-hexane, Cobalt Acetate ($Co(OAc)_2$), Copper Acetate ($Cu(OAc)_2$), Zinc Acetate ($Zn(OAc)_2$), Silica Gel 60 (0.063-0.200 mm), TLC Aluminum Sheets, Parafilm, Distilled water (H_2O).

4.2 Equipment

IR Spectrophotometer	Perkin Elmer Spectrum One FT-IR (ATR sampling accessory)
UV/ VIS Spectrophotometer	UNICAM UV2-100
Magnetic Stirrer and Heater	IKA
Elemental Analyses	Thermo Finnigan Flash EA 1112
^{1}H-NMR Spectrophotometer	Bruker Ultra Shield Plus 400 MHz
^{13}C-NMR Spectrophotometer	Bruker Ultra Shield Plus 400 MHz
Mass Spectrophotometer	Bruker Daltonics Micro-TOF and MALDI-TOF

CHAPTER 5

EXPERIMENTAL PART

5.1 Synthesis of Dithiomaleonitrile Disodium Salt

Dry and powder NaCN (10 g, 0.213 mol) was stirred in DMF (70 mL) around 10 minutes. 12.84 mL (0.213 mol) CS_2 was added into that solution drop wise with stirring in ice bath for 10 minutes. Dark brown solution was stirred for extra 10 minutes and diluted to 200 mL with isobutanol and heated until all of the contents were dissolved in solvent. The solution was filtered with vacuum filtration to remove unreacted NaCN while solution was hot. Then solution was left to cool and crystallize. Needle type brown crystals was formed and filtered by vacuum filtration. The crystals were washed with diethyl ether and dried in hood.

The obtained needle type brown crystals were dissolved in 100 mL of chloroform and the dark brown solution was filtered. The solution was left to stand for 4-5 days and precipitation occurred. The precipitate having the product and sulphur was filtered and dried. Then it was dissolved in minimum methanol that can only dissolve the product and diethyl ether was added for crystallization of the product. Yellowish crystals were filtered and washed with ether and left to dry. The product was soluble in methanol, ethanol and water and insoluble in diethyl ether, chloroform and benzene (Davison and Holm, 1967).

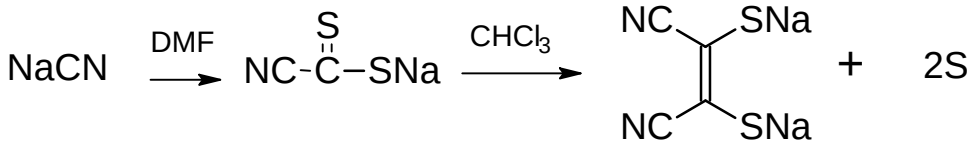


Figure 5.1 Synthesis of dithiomaleonitrile disodium salt.

5.2 Synthesis of 2,3-bis(2-anthraquinonylmethylthio) maleonitrile (2)

Disodium salt of dithiomaleonitrile (**1**) (2.80 g, 15 mmol) was mixed with 2-(chloromethyl)anthraquinone (9.63 g, 37.5 mmol) in methanol (75 mL) and refluxed under nitrogen for about 24 h. When MeOH was evaporated, the remaining product was treated with $CHCl_3$ to remove insoluble salts by filtration. The $CHCl_3$ solution was extracted several times with 15% Na_2SO_4 solution and then dried over anhydrous Na_2SO_4 overnight. After evaporation of the solvent the colored product was extracted with refluxing n-hexane to remove any excess 2-(chloromethyl)anthraquinone. The product was a brown colored and was very soluble in chloroform, dichloromethane, THF, benzene and acetone, but insoluble in n-hexane. Yield: 7.43 g (85%). FT-IR, $\nu_{max}/(cm^{-1})$: 3070 (CH, aromatic), 2978-2867 (CH, aliphatic), 2218 (C≡N), 1722, 1674 (C=O), 1612 (C=C, aromatic), 1588, 1557, 1446, 1365, 1312, 1271, 1200, 1051, 1014, 889, 845, 760, 736 (Appendix A). ^{1}H NMR (δ, ppm) 7.82-7.68 (m, 6H, Ar-H), 7.58-7.32 (m, 8H, Ar-H), 4.66 (s, 4H, S-CH_2) (Appendix B). ^{13}C NMR (δ, ppm) 40.2, 113.6, 115.8, 129.2, 130.2, 131.4, 132.2, 132.4, 133.8, 143.2, 182.4 (Appendix C). MS (ESI): (m/z): 582.1 $[M]^+$ (Appendix D). Anal. calcd. for $C_{34}H_{18}N_2S_2O_4$: C, 70.09; H, 3.11; N, 4.81%. Found: C, 70.20; H, 3.21; N, 4.70%.

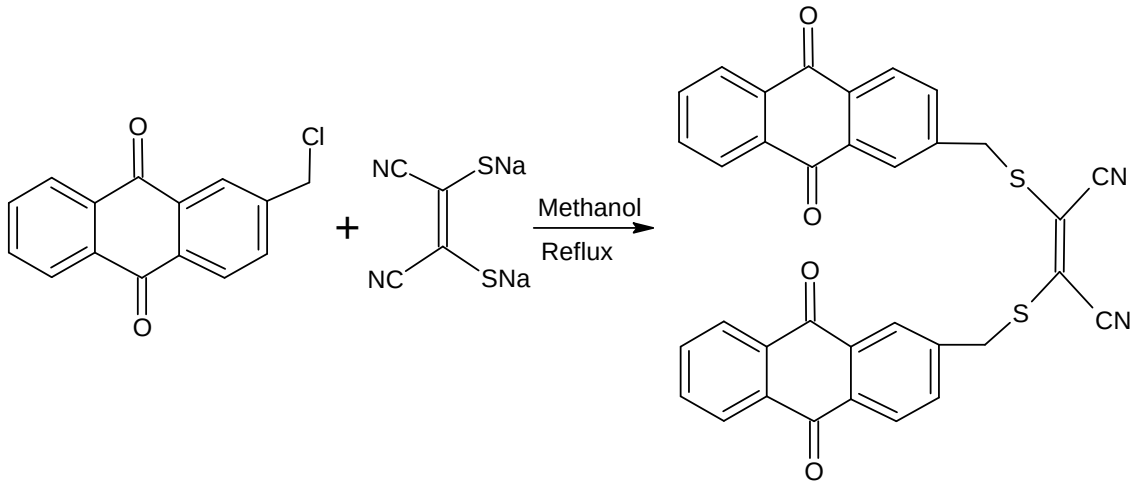


Figure 5.2 2,3-bis(2-anthraquinonylmethylthio) maleonitrile.

5.3 Synthesis of [2,3,7,8,12,13,17,18-octakis(2-anthraquinonylmethylthio) porphyrazinato] Mg(II) (3a)

Mg turnings (6 mg, 0.25 mmol) and a small I_2 crystal were refluxed in n-BuOH (20 mL) for about 8 h to obtain $Mg(BuO)_2$. **2** (291 mg, 0.5 mmol) was added to this solution and the mixture was refluxed for about 12 h. The blue-green colored product was filtered, washed with ethanol and water and dried in a vacuum. The crude product was dissolved in $CHCl_3$ and filtered. The $CHCl_3$ solution was dried over anhydrous Na_2SO_4. When the solvent was evaporated, a dark blue-green product was obtained. Finally, pure porphyrazine was obtained by chromatography on silica gel using methanol/chloroform (1:50) mixture as eluent. The product was soluble in chloroform, dichloromethane, acetone and toluene, but insoluble in *n*-hexane. Yield: 200 mg (68%). FT-IR, $\nu_{max}/(cm^{-1})$: 3053 (CH, aromatic), 2924-2880 (CH, aliphatic), 1715, 1676 (C=O), 1624 (C=C, aromatic), 1590, 1554, 1526, 1446, 1309, 1283, 1257, 1188, 1160, 1106, 1086, 963, 908, 888, 788, 758, 730, 684, 597 (Appendix E). UV-Vis. ($CHCl_3$), λ/nm (log ε / $dm^3mol^{-1}cm^{-1}$): 284 (4.88), 368 (4.64), 644 (4.45) (Appendix F & G). ^{1}H NMR (δ, ppm) 7.85-7.64 (m, 24H, Ar-H), 7.54- 7.28 (m, 32H, Ar-H), 5.49 (s, 16H, S-CH_2) (Appendix H). ^{13}C NMR (δ, ppm) 40.4, 113.4, 115.6, 129.1, 130.1, 131.3, 132.2, 132.4, 133.6, 143.0, 182.0 (Appendix I). MS (ESI): (m/z): **2353.2,** 2354.2, **2355.2** $[M]^+$ (Appendix J & K). Anal. calcd. for $C_{136}H_{72}N_8S_8O_{16}$ Mg: C, 69.36; H, 3.08; N, 4.76%. Found: C, 69.48; H, 3.00; N, 4.86%.

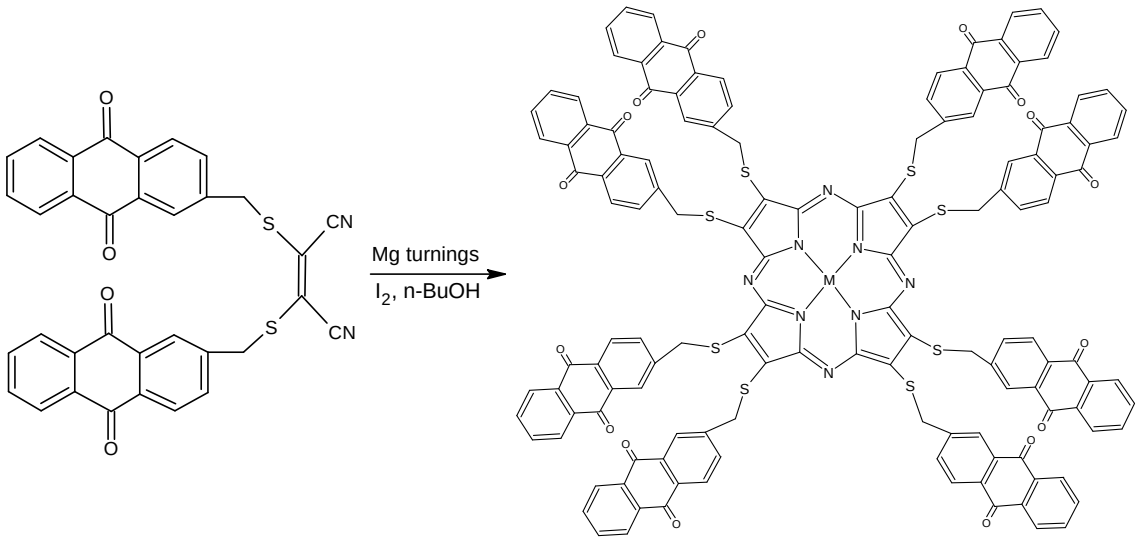


Figure 5.3 [2,3,7,8,12,13,17,18-octakis(2-anthraquinonylmethylthio) porphyrazinato] Mg(II) (3a).

5.4 Synthesis of [2,3,7,8,12,13,17,18- octakis(2-anthraquinonylmethylthio) H^{21}, H^{23} porphyrazine] (3b)

3a (235 mg, 0.1 mmol) was dissolved in the minimum amount of trifluoroacetic acid (~4 mL) and stirred for 3 h at room temperature. When the reaction mixture was added to ice drop by drop and neutralized with 25% ammonia solution, precipitation occurred and it was filtered. The precipitate was extracted into the chloroform and the chloroform solution was extracted with water twice. After drying over anhydrous Na_2SO_4, the solvent was evaporated to obtain a purple colored metal-free porphyrazine. The crude product (**3b**) was purified by chromatography on silica gel using methanol/chloroform (1:50) mixture as the eluent. Yield: 145 mg (62%). FT-IR, $\nu_{max}/(cm^{-1})$: 3282 (N-H), 3065-3019 (CH, aromatic), 2945-2863 (CH, aliphatic), 1660 (C=O), 1608 (C=C, aromatic), 1592, 1557, 1462, 1435, 1369, 1306, 1197, 1128, 1016, 986, 884, 840, 800, 732, 685 (Appendix L). UV-Vis. ($CHCl_3$), λ/nm (log ε / $dm^3mol^{-1}cm^{-1}$): 284 (4.99), 348 (4.81), 620 (4.25), 676 (4.32) (Appendix M). ^1H NMR (δ, ppm) 7.88-7.66 (m, 24H, Ar-H), 7.57- 7.30 (m, 32H, Ar-H), 5.45 (s, 16H, S-CH_2), -1.10 (br s, 2H, NH) (Appendix N). ^{13}C NMR (δ, ppm) 40.4, 113.3, 115.5, 129.1, 130.0, 131.4, 132.3, 132.5, 133.5, 143.1, 182.1. MS (ESI): (m/z): 2333.2 $[M]^+$. Anal. calcd. for $C_{136}H_{74}N_8S_8O_{16}$: C, 70.03; H, 3.20; N, 4.80%. Found: C, 70.14; H, 3.11; N, 4.69%.

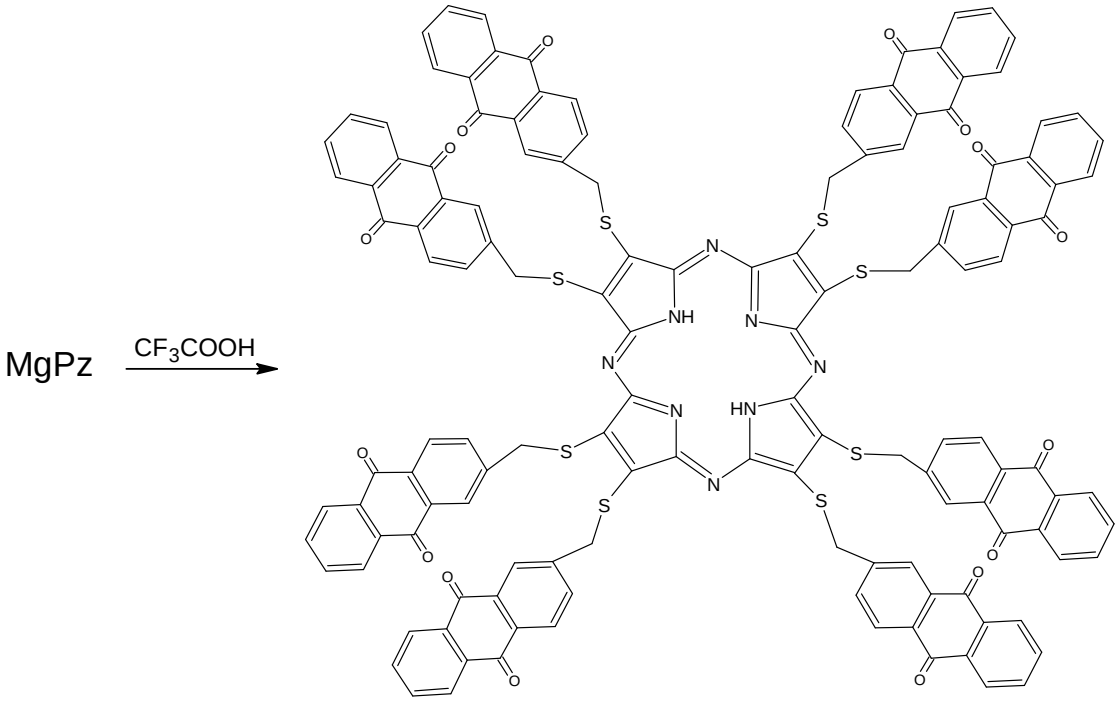


Figure 5.4 [2,3,7,8,12,13,17,18-octakis(2-anthraquinonylmethylthio) H^{21}, H^{23} porphyrazine] (3b).

5.5 General procedure for metallo-porphyrazines (3c-3e)

3b (233 mg, 0.1 mmol) in $CHCl_3$ (10 mL) was stirred with the metal salt [$Cu(OAc)_2$ (181.6 mg, 1 mmol), $Zn(OAc)_2$ (183.4 mg, 1 mmol) or $Co(OAc)_2$ (177 mg, 1 mmol)] in ethanol (15 mL) and refluxed under nitrogen for about 6 h. Then, the precipitate composed of the crude product and the excess metal salt was filtered. The precipitate was treated with $CHCl_3$ and the insoluble metal salts were removed by filtration. The filtrate was reduced to the minimum volume under reduced pressure and then added into *n*-hexane (100 mL) drop by drop to realize the precipitation. Finally, pure porphyrazine derivatives were obtained by chromatography on silica gel using methanol/chloroform (1:100) mixture as the eluent.

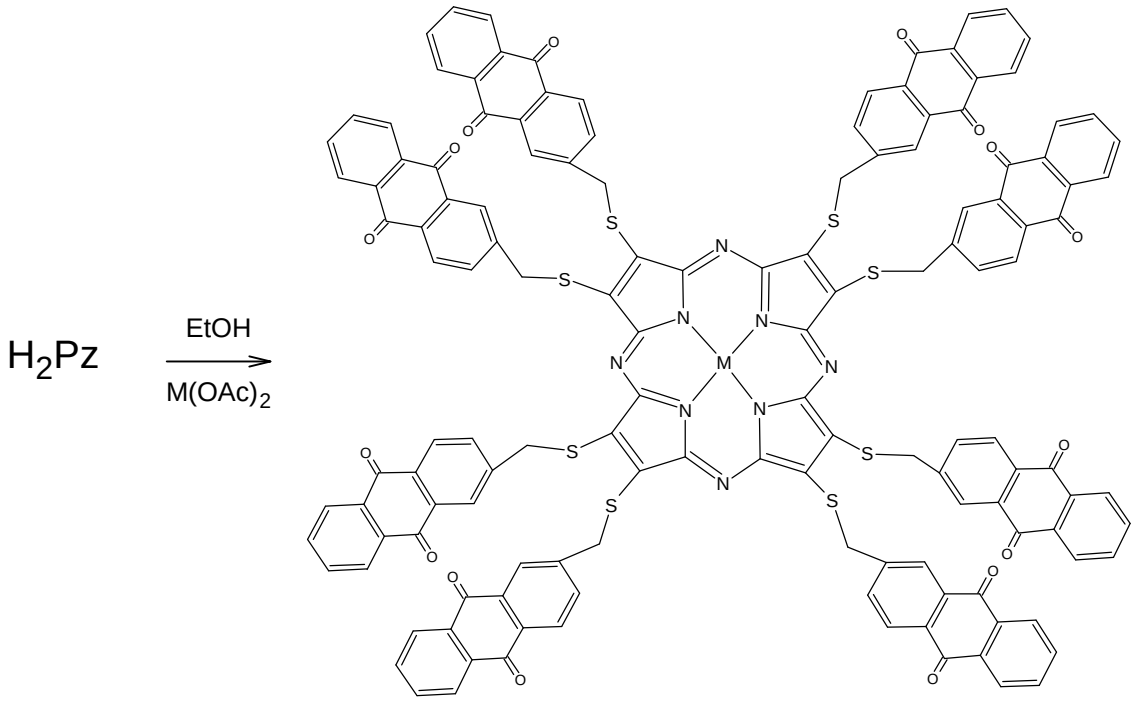


Figure 5.5 [2,3,7,8,12,13,17,18-octakis(2-anthraquinonylmethylthio) porphyrazinato] {M=Cu(II), Zn(II) or Co(II)}(3c-3e).

5.6 [2,3,7,8,12,13,17,18-octakis(2-anthraquinonylmethylthio) porphyrazinato] Cu(II) (3c)

Yield: 115 mg (48%). FT-IR, ν_{max}/(cm^{-1}): 3072 (CH, aromatic), 2984-2870 (CH, aliphatic), 1676 (C=O), 1618 (C=C, aromatic), 1592, 1557, 1450, 1369, 1312, 1271, 1168, 1126, 1026, 986, 846, 761, 733, 711, 655. UV-Vis. ($CHCl_3$), λ/nm (log ε / $dm^3mol^{-1}cm^{-1}$): 284 (4.96), 344 (4.79), 632 (4.39) (Appendix O). MS (ESI): (m/z): 2394.9, **2395.9** $[M]^+$ (Appendix P & Q). Anal. calcd. for $C_{136}H_{72}N_8S_8O_{16}Cu$: C, 68.23; H, 3.03; N, 4.68%. Found: C, 68.32; H, 3.13; N, 4.58%.

5.7 [2,3,7,8,12,13,17,18-octakis(2-anthraquinonylmethylthio) porphyrazinato] Zn(II) (3d)

Yield: 125 mg (52%). FT-IR, ν_{max}, cm^{-1}: 3062 (CH, aromatic), 2966-2875 (CH, aliphatic), 1675 (C=O, aromatic), 1618 (C=C, aromatic), 1595, 1553, 1455, 1366, 1315, 1274, 1170, 1129, 1024, 985, 844, 765, 736, 714, 658. UV-Vis. ($CHCl_3$), λ/nm (log ε / $dm^3mol^{-1}cm^{-1}$): 288 (4.97), 344 (4.88), 644 (4.65) (Appendix R). ^{1}H NMR (δ, ppm) 7.84-7.60 (m, 24H, Ar-H), 7.56- 7.25 (m, 32H, Ar-H), 4.75 (s, 16H, S-CH_2).
^{13}C NMR (δ, ppm) 40.2, 113.6, 115.8, 129.2, 130.3, 131.0, 132.0, 132.2, 133.8, 143.3, 182.4. MS (ESI): (m/z): **2394.8,** 2396.8, **2397.8, 2398.8, 2400.8** $[M]^+$ (Appendix S & T). Anal. calcd. for $C_{136}H_{72}N_8S_8O_{16}Zn$: C, 68.18; H, 3.03; N, 4.68%. Found: C, 68.09; H, 3.12; N, 4.79%.

5.8 [2,3,7,8,12,13,17,18-octakis(2-anthraquinonylmethylthio) porphyrazinato] Co(II) (3e)

Yield: 131 mg (55%). FT-IR, ν_{max}, cm^{-1}: 3066 (CH, aromatic), 2968-2870 (CH, aliphatic), 1675 (C=O, aromatic), 1612 (C=C, aromatic), 1595, 1552, 1455, 1364, 1315, 1272, 1170, 1127, 1024, 984, 844, 767, 736, 712, 658. UV-Vis. ($CHCl_3$), λ/nm (log ε / $dm^3mol^{-1}cm^{-1}$): 288 (4.94), 340 (4.82), 640 (4.47) (Appendix U). MS (ESI): (m/z): 2390.2 $[M]^+$. Anal. calcd. for $C_{136}H_{72}N_8S_8O_{16}Co$: C, 68.36; H, 3.04; N, 4.69%. Found: C, 68.47; H, 3.16; N, 4.58%.

CHAPTER 6

RESULTS AND DISCUSSIONS

New soluble porphyrazines with eight (2-anthraquinonylmethylthio) substituents appending to the peripheral positions have been synthesized and characterized. The starting point for these new porphyrazine structures with eight (2-anthraquinonylmethylthio) functional groups bound to the peripheral is 2,3-bis(2-anthraquinonylmethylthio)maleonitrile (**2**) which was obtained from the disodium salt of dithiomaleonitrile (**1**) and I_2. The brown colored product (**2**) was obtained in yield 85%.

In order to convert the 2,3-bis(2-anthraquinonylmethylthio)maleonitrile (**2**) into porphyrazine (**3a**) (Fig 6.1), we have made use of its template reaction in the presence of magnesium butanolate, which is the typical method generally applied in cyclotetramerization of these tetrapyrrole derivatives (Wolf, Degener et al., 1960 ; Kopranenkov, Goncharova et al., 1979 ; Schramm and Hoffman, 1980). The dark green colored (**3a**) was obtained with a yield of 68% (Fig. 6.1). **3a** was soluble in chloroform, dichloromethane, acetone and toluene, but insoluble in *n*-hexane.

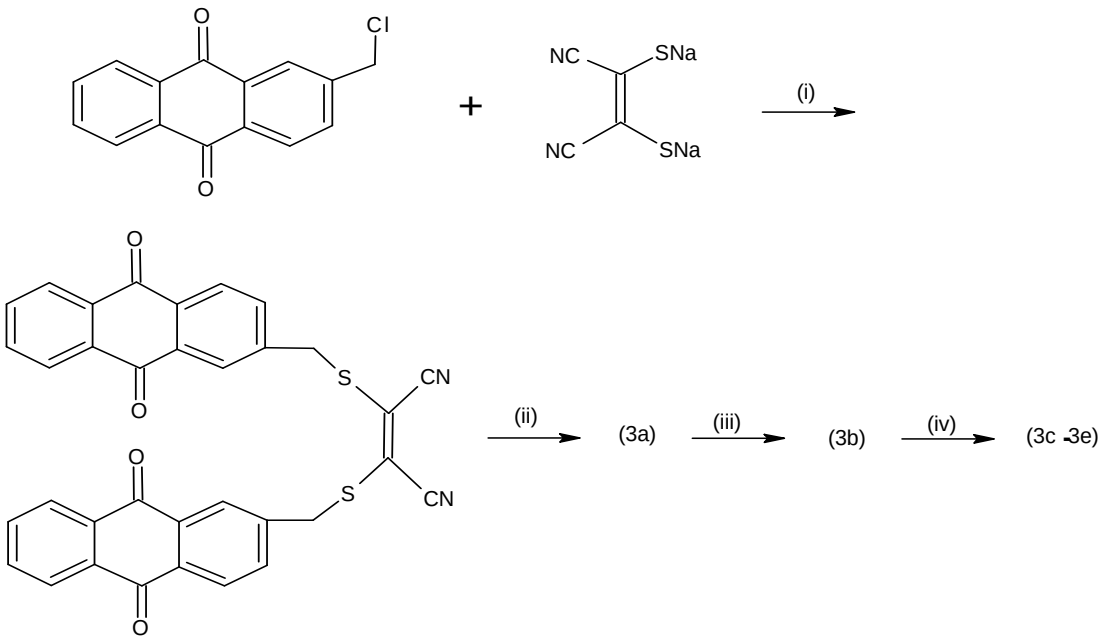
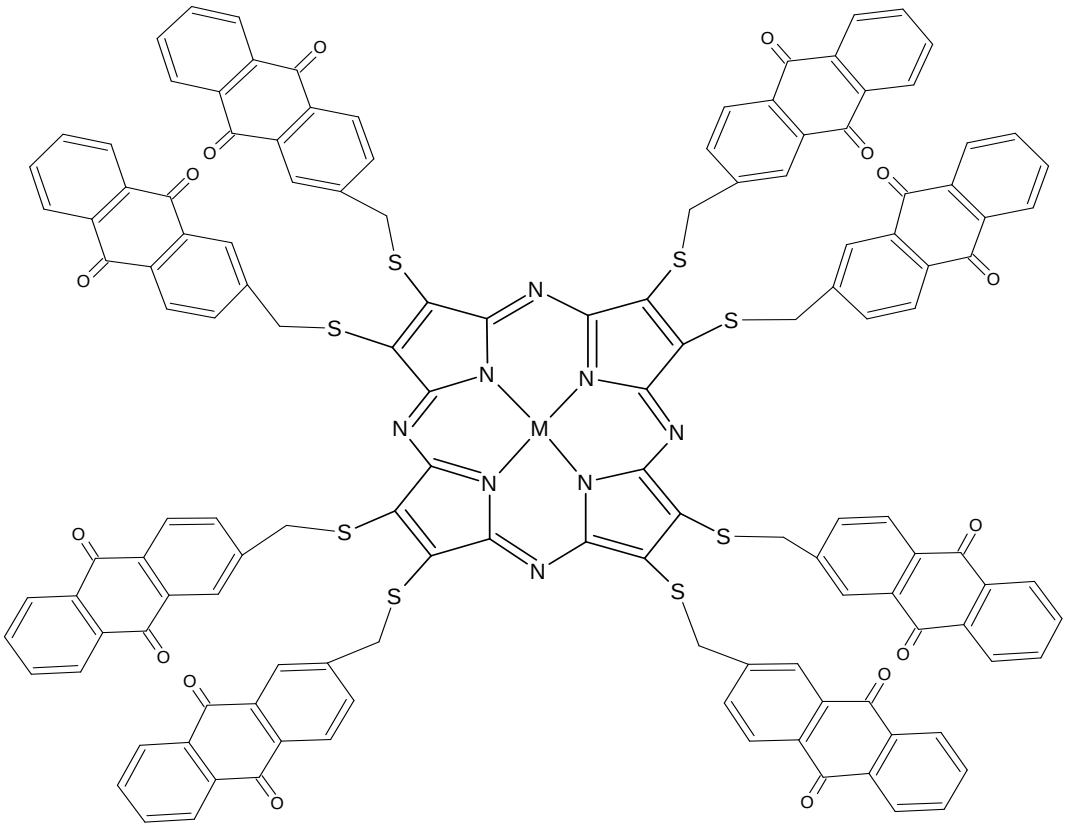


Figure 6.1 (**i**) Methanol; (**ii**) Mg turnings, I_2, n-BuOH; (**iii**) CF_3CO_2H; (**iv**) EtOH and $Cu(OAc)_2$, $Zn(OAc)_2$, or $Co(OAc)_2$.



M= Mg (**3a**); 2H (**3b**); Cu (**3c**); Zn (**3d**); Co (**3e**)

Figure 6.2 Octakis (2-anthraquinonylmethylthio) substituted porphyrazines (**3a-3e**).

The conversion of **3a** to metal-free derivative **3b** was achieved by the treatment with trifluoroacetic acid followed by neutralization with ammonia and aqueous precipitation. The mass spectral results have clearly indicated the change of the structure from magnesium porphyrazinate (**3a**) to the demetalated porphyrazine (**3b**). Incorporation of transition metal ions into the inner core of porphyrazine (**3c-3e**) was achieved by treatment of the demetalated porphyrazine (**3b**) with metal acetates [i.e. $Cu(OAc)_2$, $Zn(OAc)_2$ or $Co(OAc)_2$]. The metallation reactions were completed by refluxing under nitrogen for about 4 h in a chloroform-ethanol mixture. Elemental analyses correspond closely with the values calculated for (**2, 3a-3e**) (Table 6.1).

Table 6.1 Elemental analyses results of **2** and (**3a-3e**)*****.

Compound	**C**	**H**	**N**
2	70.20 (70.09)	3.21 (3.11)	4.70 (4.81)
3a	69.48 (69.36)	3.00 (3.08)	4.86 (4.76)
3b	70.14 (70.03)	3.11 (3.20)	4.69 (4.80)
3c	68.32 (68.23)	3.13 (3.03)	4.58 (4.68)
3d	68.09 (68.18)	3.12 (3.03)	4.79 (4.68)
3e	68.47 (68.36)	3.16 (3.04)	4.58 (4.69)

* Required values are given in parentheses

In the FT-IR spectrum of **2**, the stretching vibration of C≡N is observed at 2218 cm^{-1}, the aliphatic and aromatic C-H peaks are in the range 2978-3070 cm^{-1}, C=O peak is at 1722 and 1674 cm^{-1} and C=C aromatic peak is at 1612 cm^{-1}. These values comply with those reported in the literature for similar compounds (Gonca, Köseoğlu et al., 2004 ; Gonca, 2008 ; Uslu and Gül, 2000 ; Cenan and Gonca, 2008 ; Polat and Gül, 2000). After the conversion of **2** to the porphyrazine **3a**, the sharp C≡N vibration around 2218 cm^{-1} disappeared. The N-H stretching absorptions of the inner core of the demetalated porphyrazine (**3b**) were observed around 3282 cm^{-1}. The FT-IR spectra of all porphyrazines derivatives (**3a-e**) showed that the aliphatic and aromatic C-H peaks are around 2863-3072 cm^{-1} (Uslu and Gül, 2000 ; Keskin, Köseoğlu et al., 2008 ; Gonca and Keskin, 2009 ; Nazlı, Gonca et al., 2006).

In the ^{1}H-NMR spectra of **2**, **3a**, **3b** and **3d** chemical shifts corresponding to (2-anthraquinonylmethylthio) groups came out at the expected values. The N-H protons of the metal-free porphyrazine (**3b**) were identified in the ^{1}H NMR spectrum with a broad

peak at δ = -1.10 ppm, presenting the typical shielding of inner core protons, which is a common feature of the ^{1}H NMR spectra of metal-free porphyrazines (Gonca, Köseoğlu et al., 2004 ; Cenan and Gonca, 2008 ; Sağlam and Gül, 2001 ; Rio, Rodriguez-Morgade et al., 2008). In the ^{1}H-NMR spectra of diamagnetic porphyrazines (**3a**, **3b**, **3d**), two different types of protons are clearly seen: a multiplet around 7.25-7.88 ppm corresponding to anthraquinonyl-protons and a singlet around 5.49 ppm (**3a**), 5.45 ppm (**3b**) or 4.75 ppm (**3d**) for methylene protons. The ratio of the integral values 7:2 also confirms the proposed structure. In the ^{13}C NMR spectra of diamagnetic porphyrazines **3a**, **3b** and **3d,** eleven different single chemical shifts for carbon atoms are clearly seen.

UV-vis spectra were specifically applicable to establish the structure of the porphyrazines (**3a-e**). The electronic spectra of **3a**, **3c**, **3d and 3e** exhibit a strong absorption between 632-644 nm which is due to a π-π* transition and is commonly referred to as Q band. A second intense and broad π-π* transition in the range 340-368 nm which is called B band is also a characteristic of these porphyrazine structures. As expected, the demetalated porphyrazine (**3b**) shows a splitted Q band because of the change in symmetry from D_{4h} in **3a** to D_{2h} in **3b**. Here, in the case of porphyrazines with appending (2-anthraquinonylmethylthio) substituents in addition to these absorptions of the porphyrazine core, an intense absorption due to the π→ π* transition of anthraquinone groups appeared for all these porphyrazines derivatives (**3a-e**) in the UV region around 284-288 nm (Table 6.2). UV-Vis spectra of (**3a-3e**) at a concentration of $1x10^{-5}$ M in chloroform are shown in Fig. 6.2. An absorbance *vs.* concentration study indicated that due to (2-anthraquinonylmethylthio) units, the aspect of the UV-Vis spectrum of the free ligand in Fig. 6.2, with broad and low intensity Q-bands does not exclude the presence of aggregation. UV-Vis spectra of **3a** in solvents of different polarity (chloroform, dichloromethane, acetone and toluene) are given in Fig. 6.3. There is almost no difference with respect to the changes in the nature of the solvent.

Table 6.2 UV-Vis Data for (**3a-3e**) in $CHCl_3$.

Compound	**λ/nm (log ε / dm^{3} mol^{-1} cm^{-1})**			
3a	284 (4.88)	368 (4.64)	644 (4.45)	
3b	284 (4.99)	348 (4.81)	620 (4.25)	676 (4.32)
3c	284 (4.96)	344 (4.79)	632 (4.39)	
3d	288 (4.97)	344 (4.88)	644 (4.65)	
3e	288 (4.94)	340 (4.82)	640 (4.47)	

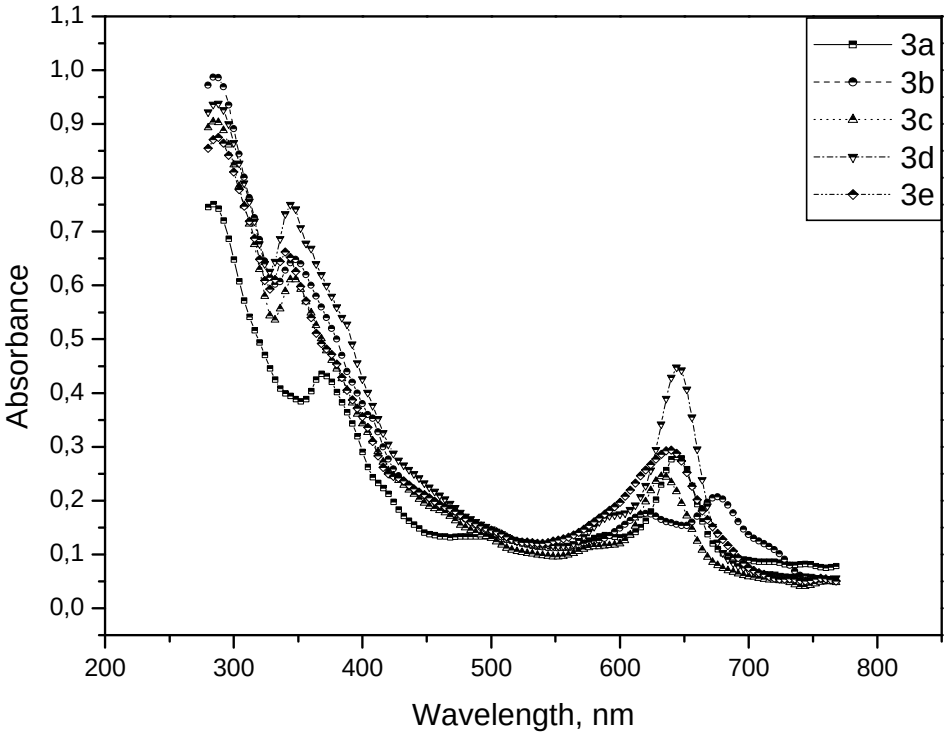


Figure 6.3 UV-Vis Spectra of (**3a-3e**) in $CHCl_3$.

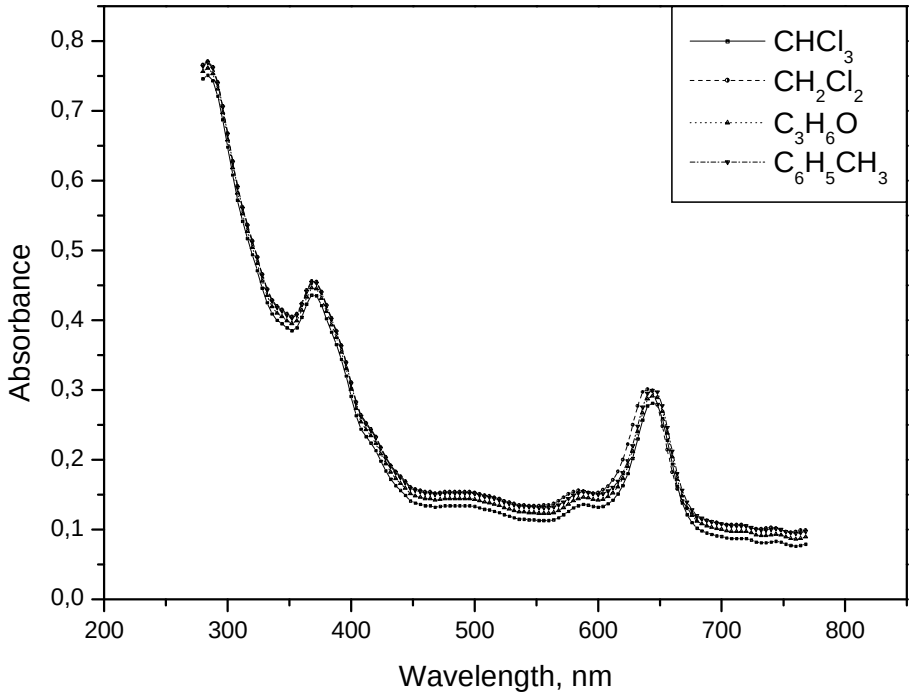


Figure 6.4 UV-Vis Spectra of **3a** in Various Solvents.

The mass spectra of **2** and (**3a-3e**) correspond closely with the real values. The mass spectra of MgPz (Fig. 6.5), CuPz (Fig. 6.6) and ZnPz (Fig. 6.7) were rearranged by representing the significant isotopes of each one (Table 3-5).

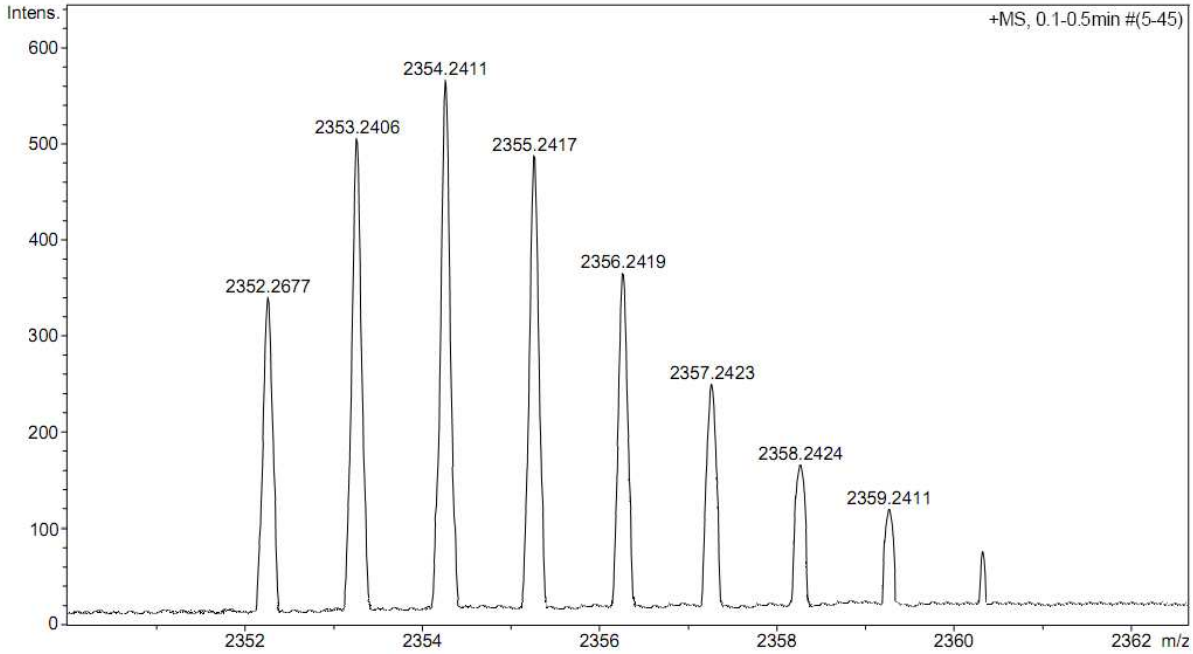


Figure 6.5 Mass Spectrum of MgPz (**3a**).

Table 6.3 Isotopes of Magnesium.

nuclide symbol	**Z(p)**	**N(n)**	**isotopic mass (u)**	**half-life**	**nuclear spin**	**representative isotopic composition (mole fraction)**	**range of natural variation (mole fraction)**
	excitation energy						
^{24}Mg	12	12	23.985041700(14)	Stable	0+	0.7899(4)	0.78958-0.79017
^{25}Mg	12	13	24.98583692(3)	Stable	5/2+	0.1000(1)	0.09996-0.10012
^{26}Mg	12	14	25.982592929(30)	Stable	0+	0.1101(3)	0.10987-0.11030

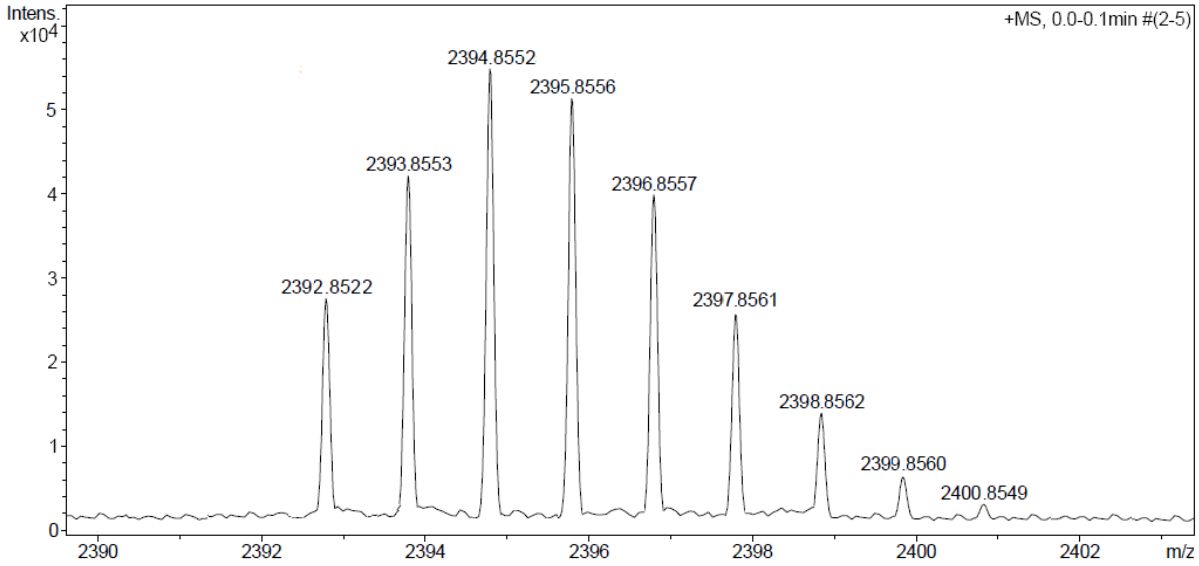


Figure 6.6 Mass Spectrum of CuPz (**3c**).

Table 6.4 Isotopes of Copper.

nuclide symbol	Z(p)	N(n)	isotopic mass (u)	half-life	nuclear spin	representative isotopic composition (mole fraction)	range of natural variation (mole fraction)
	excitation energy						
^{63}Cu	29	34	62.9295975(6)	STABLE	3/2-	0.6915(15)	0.68983-0.69338
^{65}Cu	29	36	64.9277895(7)	STABLE	3/2-	0.3085(15)	0.30662-0.31017

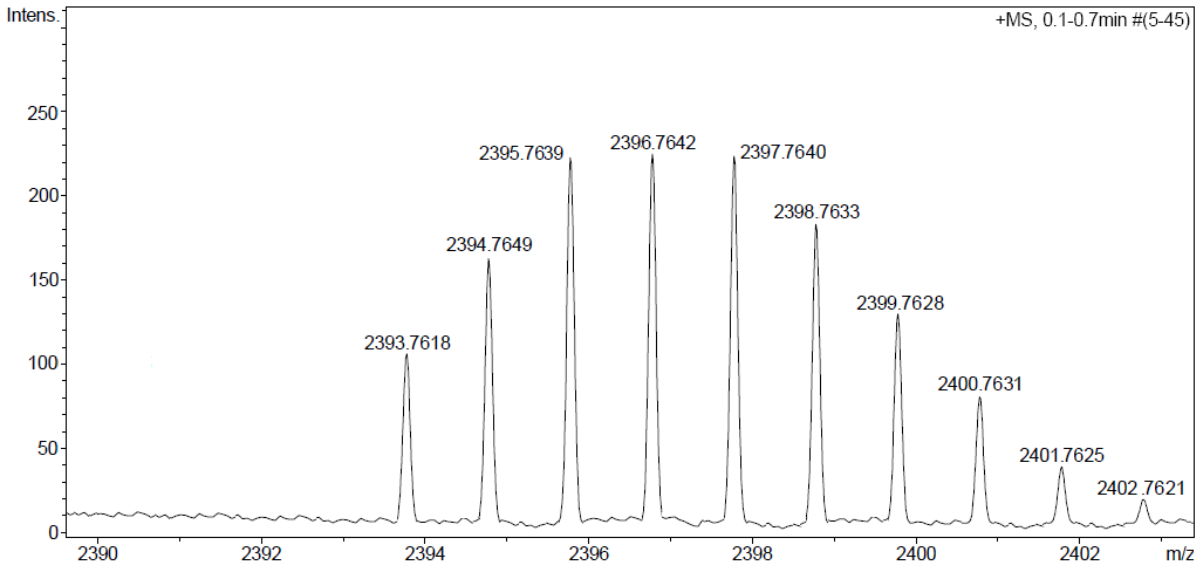


Figure 6.7 Mass Spectrum of ZnPz (**3d**).

Table 6.5 Isotopes of Zinc.

nuclide symbol	Z(p)	N(n)	isotopic mass (u)	half-life	nuclear spin	representative isotopic composition (mole fraction)	range of natural variation (mole fraction)
	excitation energy						
^{64}Zn	30	34	63.9291422(7)	STABLE [>2.3E+18 a]	0+	0.48268(321)	
^{66}Zn	30	36	65.9260334(10)	STABLE	0+	0.27975(77)	
^{67}Zn	30	37	66.9271273(10)	STABLE	5/2-	0.04102(21)	
^{68}Zn	30	38	67.9248442(10)	STABLE	0+	0.19024(123)	
^{70}Zn	30	40	69.9253193(21)	STABLE [>1.3E+16 a]	0+	0.00631(9)	

In conclusion, we have described the synthesis and the spectral characterization of new porphyrazines surrounded with eight bulky (2-anthraquinonylmethylthio) groups on the periphery. High electron density on the substituents results with a second absorption in the ultraviolet region of comparable intensity as the intense B band of porphyrazines.

REFERENCES

Ahsen, V., E. Yılmazer, A. Gürek, A. Gül, and Ö. Bekaroğlu, *Helv. Chim. Acta*., Vol. 71, pp. 1616, 1988.

Akkuş, H., and A. Gül, *Trans. Met. Chem*., Vol. 26, pp. 689, 2001.

Anderson, M. E., A. G. M. Barrett, and B. M. Hoffman, *Inorg. Chem*., Vol. 38, pp. 6143, 1999.

Anderson, M. E., R. L. Letsinger, A. G. M. Barrett, and B. M. Hoffman, *J. Inorg. Biochem*., Vol. 80, pp. 257, 2000.

Antipas, A., D. Dolphin, M. Gouterman, and E.C. Johnson, *J. Am. Chem. Soc*., Vol. 100, pp. 7705, 1978.

Baguley, M. E., H. France, R.P. Linstead, and M. Whalley, *J. Chem. Soc*., Vol. 35, pp. 21, 1955.

Banfi, S., F. Montanari, S. Quici, S. V. Barkanova, O. L. Kaliya, V. N. Kopranenkov, and E. A. Luk'yanets, *Tetrahedron Lett*., Vol. 36, pp. 2317, 1995.

Barrett, P. A., D. A. Frye, and R. P. Linstead, *J. Chem. Soc*., pp. 1157–1165, 1938.

Baumann, T.F., A.G.M. Barrett, and B.M. Hoffman, *Inorg. Chem*., Vol. 36, pp. 5661, 1997.

Beall, L. S., N. S. Mani, A. J. P. White, D. J. Williams, A. G. M. Barrett, and B. M. Hoffman, *J. Org. Chem*., Vol. 63, pp. 5806, 1998.

Bordbar, A. K., M. Davari, E. Safaei, and V. Mirkhani, *J. Porphyrins Phthalocyanines*, Vol. 11, pp. 139, 2007.

Capobianchi, A. C. Ercolani, A. M. Paoletti, G. Pennesi, G. Rossi, A. Chiesi-Villa, and C. Rizzoli, *Inorg. Chem*., Vol. 32, pp. 4605-4611, 1993.

Cenan, N., and E. Gonca, *J. Chem. Res*., Vol. 12, pp. 693, 2008.

Chandrasekharam, M., C. S. Rao, P. S. Surya, M. L. Kantam, M. R. Reddy, P. Y. Reddy, and T. Toru, *Tetrahedron Lett*., Vol. 48, pp. 2627, 2007.

Chen, Y., L. Huang, M.A. Ranade, and X.P. Zhang, *J. Org. Chem*., Vol. 68, pp. 3714, 2003.

Choi, C., P. Tsang, J. Huang, E.Y.M. Chan, W. Ko, W. Fong, and D.K.P. Ng, *Chem. Commun*., Vol. 19, pp. 2236, 2004.

Clarkson, G. J., A. Cook, N. B. McKeown, K. E. Treacher, and Z. Ali-Adib, "*Macromolecules*", Vol. 29, pp. 913–917, 1996.

Cook, M.J., and A. Jafari-Fini, "*Tetrahedron*", Vol. 56, pp. 4085, 2000.

Davison, A., and R.H. Holm, *Inorg. Synth*., Vol. 10, pp. 8, 1967.

de la Torre, G., C. G. Claessens, and T. Torres, Eur. *J. Org. Chem*., pp. 2821–2830, 2000.

Deng, K., F. Huang, D. Wang, Z. Peng, and Y. Zhou, *Chem. Lett*., Vol. 33, pp. 34, 2004.

Donzello, M. P., D. Dini, G. D'Arcangelo, C. Ercolani, R. Zhan, Z. Ou, P. A. Stuzhin, and K. M. Kadish, *J. Am. Chem. Soc*., Vol. 125, pp. 14190, 2003.

Ehrlich, L. A., P. J. Skrdla, W. K. Jarrell, J. W. Sibert, N. R. Armstrong, S. S. Saavedra, A. G. M. Barrett, and B. M. Hoffman, *Inorg. Chem*., Vol. 39, pp. 3963-3969, 2000.

Erdoğmuş, A., A. Koca, U. Avciata, and A. Gül, *Z. Anorg. Allg. Chem*., Vol. 634, pp. 2469, 2008.

Ertem, B., A. Bilgin, H. Kantekin, and Y. Gök,"*Polyhedron*", Vol. 27, pp. 2186, 2008.

Fischer and Endermann F., *Ann. Chem*., Vol. 531, pp. 245, 1937.

Fuchter, M. J., C. Zhong, H. Zong, B. M. Hoffman, and A. G. M. Barrett, Aust. *J. Chem*., Vol. 61, pp. 235–255, 2008.

Fuchter, M. J., L. S. Beall, S. Baum, A. G. Montalban, E. G. Sakellariou, N. S. Mani, T. Miller, A. J. P. White, D. J. Williams, A. G. M. Barrett, and B. M. Hoffman, "*Tetrahedron*", Vol. 61, pp. 6115, 2005.

Geyer, M., F. Plenzig, J. Rauschnabel, M. Hanack, B. del Rey, A. Sastre, and T. Torres, *Synthesis*, pp. 1139-1151, 1996.

Gonca, E., and A. Gül, *Inorg. Chem*. Commun., Vol. 8, pp. 343, 2005.

Gonca, E., and B. Keskin, *J. Coord. Chem*., Vol. 62, pp. 2875-2882, 2009.

Gonca, E., *J. Chem. Res*., Vol. 2008, pp. 465, 2008.

Gonca, E., Trans. *Met. Chem*., Vol. 33, pp. 547, 2008.

Gonca, E., Ü.G. Baklacı, and H.A. Dinçer, *J. Porphyrins Phthalocyanines*, Vol. 12, pp. 116, 2008.

Gonca, E., Ü.G. Baklacı, and H.A. Dinçer, "*Polyhedron*", Vol. 27, pp. 2431, 2008.

Gonca, E., Y. Köseoğlu, B. Aktaş, and A. Gül, "*Polyhedron*", Vol. 23, pp. 1845-1849, 2004.

Guinchard, X., M. J. Fuchter, A. Ruggiero, B. J. Duckworth, A. G. M. Barrett, and B. M. Hoffman, *Org. Lett*., Vol. 9, pp. 5291, 2007.

Hachiya, S., A. S. Cook, D. B. G. Williams, A. G. Montalban, A. G. M. Barrett, and B. M. Hoffman, "*Tetrahedron"*, Vol. 56, pp. 6565, 2000.

Hanack, M., and G. Renz, *Chem. Ber*., Vol. 123, pp. 1105, 1990.

Hasanov, B., and A. Gül, Synth. React. *Inorg. Met.-Org. Chem*., Vol. 31, pp. 673, 2001.

Haywood-Small, S. L., D. I. Vernon, J. Griffiths, J. Schofield, and S. B Brown, *Biochem. Biophys. Res. Commun.*, Vol. 339, pp. 569-76, 2006.

Hirohashi, R., K. Sakamoto, and E. Ohno-Okumura, *Phthalocyanines as Functional Dyes*, ICP, Tokyo, Japan, 2004.

Janczak, J., and R. J. Kubiak, *Chem. Soc*., Dalton Trans., pp. 2539-2543, 1994.

Kadish, K. M., and K. M. Smith, R. Guilard, *In The Porphyrin Handbook*, Eds., Academic Press, Boston, Vol. 1, pp. 1–43, 1999.

Kaliya, O. L., and E. A. Luk'yanets, in "*Fundamental Research in Homogeneous Catalysis*", Ed. A. E. Shilov, Gordon and Breach Sci. Publ., New York, London, Vol. 1, pp. 335, 1986.

Kavran, G., H. Akkuş, A. Gül, and F.B. Erim, *J. Sep. Sci*., Vol. 25, pp. 1, 2002.

Kemikli, N., and R. Öztürk, *Inorg. Chem*. Commun., Vol. 11, pp. 338, 2008.

Keskin, B., Y. Köseoğlu, U. Avcıata, and A. Gül, "*Polyhedron*", Vol. 27, pp. 1155, 2008.

Khelevina, O.G., and S.V. Rumyantseva, "*Advances in Porphyrin Chemistry*", Golubchikov O.A., Ed., St. Petersburg: NII Khimii SPbGU, Vol. 4, pp. 128, 2004.

Khelevine, O.G., Y.V. Romanenko, and M.K. Islyaikin, *J. Coord. Chem*., Vol. 33, pp. 155, Russ., 2007.

Kobayashi, N. S., T. Nakajima, and T. Osa, *Inorg. Chim*. Acta., Vol. 210, pp. 131–133, 1993.

Kobayashi, N., C.C. Leznoff, and A.B.P. Lever (Eds.), "*Phthalocyanines Properties and Applications*", Vol. 2, pp. 104, 1993.

Kopranenkov, V.N., and E.A. Luk'yanets, "*Russian Chemical Bulletin*", Vol. 44, pp. 2216, 1995.

Kopranenkov, V.N., L.S. Goncharova, and E.A. Luk'yanets, *J. Org. Chem*., Vol. 15, pp. 1076, 1979.

Kudrevich, S. V., and J. E. van Lier, *Coord. Chem*. Rev., Vol. 156, pp. 163–182, 1996.

Kudrevich, S., N. Brasseur, C. LaMadeleine, S. Gilbert, and J. E. van Lier, *J. Med. Chem*., Vol. 40, pp. 3897–3904, 1997.

Lei, Y. P., J. Sun, C. J. Yang, K. Deng, and D. Y. Wang, *J. Porphyrins Phthalocyanines*, Vol. 9, pp. 537, 2005.

Leznoff, C. C. and A. B. P. Lever, "*Phthalocyanines: Properties and Applications*", VCH Publ., New York, San Francisco, London, pp. 1-3, 1993.

Leznoff, C. C., A. M. D'Ascanio, and S. Z. Yildiz, *J. Porphyrins Phthalocyanines*, Vol. 4, pp. 103–111, 2000.

Leznoff, C.C., and A.B.P. Lever (Eds.), "*Phthalocyanines: Properties and Applications*", VCH Publishers, New York, pp. 1-4, 1990-1996.

Leznoff, C.C., S.M. Marcuccio, S. Greenberg, and A.B.P. Lever, *J. Chem*, Vol. 63, pp. 623, Can., 1985.

Linßen, T.G., and M. Hanack, *Chem. Ber*., Vol. 127, pp. 2051, 1994.

Linstead, R. P. and M. Whalley, *J. Chem. Soc*., pp. 4839, 1952.

Lui, M., D. Z. Han, K. Deng, and D. Y. Wang, *J. Catal*, Vol. 25, pp. 834, Chin., 2004.

Mbatha, B.G., PhD. Thesis in University of Johannesburg, 2006.

Mbatha, B.G., "*Solubilisation of Porphyrins used in Photodynamic Therapy of Cancer*", M.S. Thesis, University of Transkei, 1999.

McCleverty, J.A., and T.J. Meyer (Eds), *Comprehensive Coordination Chemistry II*, Vol. 9, Elsevier, Amsterdam, 2004.

McKeown, N. B., and S. Weinreb, "*Science of Synthesis*", Ed., Georg Thieme Verlag, Stuttgart, Germany, Vol. 17, 2003.

McKeown, N.B., *Adv. Mater*., Vol. 11, pp. 67, 1999.

McKeown, N.B., *Phthalocyanine Materials*, Cambridge University Press, Cambridge, 1998.

Michel S. L., S. Baum, A. G. M. Barrett, and B. M. Hoffman, in *Progress in Inorganic Chemistry* (Ed. Karlin K. D.), J. Wiley & Sons: NewYork, NY, Vol. 50, pp. 473, 2001.

Mikhalenko, S. A., E. V. Korobkova, and E. A. Luk'yanets, Zh. Obshch. *Khim*., Vol. 40, pp. 400, 1970.

Miller, J. D., E. D. Baron, H. Scull, A. Hsia, J. C. Berlin, T. McCormick, V. Colussi, M. E. Kenney, K. D. Cooper, and N. L. Oleinick, Toxicol. *Appl. Pharmacol*., Vol. 224, pp. 290-9, 2007.

Miwa, H., and N. Kobayashi, *Chem. Lett*., pp. 1303–1304, 1999.

Mockert, H., D. Schmeisser, and W. Gbpel, *Sensors Acctuators*, Vol. 29, pp. 159, 1989.

Montalban, A. G., S. Baum, B. M. Hoffman, and A. G. M. Barrett, *J. Chem. Soc*., Dalton Trans., pp. 2093, 2003.

Mørkved, E. H., H. Kjosen, H. Ossletten, and N. Erchak, *J. Porphyrins Phthalocyanines*, Vol. 3, pp. 417–423, 1999.

Moser, F. H., and A. L. Thomas, "*The Phthalocyanines*", CRC Press, Boca Raton (Fla.), Vol. 1, pp. 2, 1983.

Nazlı, A., E. Gonca, and A. Gül, *J. Porphyrins Phthalocyanines*, Vol. 10, pp. 996, 2006.

Nevin, W.A., W. Liu, S. Greenberg, M.R. Hempstead, S.M. Marcuccio, M. Melník, C.C. Leznoff, and A.B.P. Lever, *Inorg. Chem*., Vol. 26, pp. 891, 1987.

Ogunsipe, A., J. Chen, and T. Nyokong, New J. *Chem*., Vol. 28, pp. 1, 2004.

Okur, A.İ., A. Gül, A. Cihan, N. Tan, Ö. Bekaroğlu, Synth. React. *Inorg. Met.-Org. Chem.* Vol. 20, pp. 1399, 1990.

Okura, I., "*Photosensitization of Porphyrins and Phthalocyanines*", Kodansya, Tokyo, Japan, 2000.

Öztürk, R., and A. Gül, *Tetrahedron Lett*., Vol. 45, pp. 947, 2004.

Pankow, J. W., C. Arbour, J. P. Dodelet, G. E. Collins, and N. R. Armstrong, *J. Phys. Chem*., Vol. 97, pp. 8485-8494, 1993.

Petrov, O. A., Russ. J. *Coord. Chem*., Vol. 27, pp. 449, 2001.

Polat, M., and A. Gül, "*Dyes and Pigments*", Vol. 45, pp. 195, 2000.

Price, R. Metal Complexes of Azo Compounds, *In Comprehensive Coordination Chemistry*; G. Wilkinson, Ed.; Pergamon, Oxford, UK, Vol. 6, pp. 40-77, 1987.

Pullen, A.E., C. Faulmann, and P. Cassoux, Eur. J. *Inorg. Chem*., pp. 269, 1999.

Rio, Y., M. S. Rodriguez-Morgade, and T. Torres, *Org. Biomol. Chem*., Vol. 6, pp. 1877, 2008.

Rodriguez-Morgade, M. S., and P. A. Stuzhin, *J. Porphyrins Phthalocyanines*, Vol. 8, pp. 1129, 2004.

Sağlam, Ö., and A. Gül, "*Polyhedron*", Vol. 20, pp. 269-275, 2001.

Sakamoto, K., T. Kato, E. Ohno-Okumura, M. Watanabe, and M. J. Cook, *Dyes and Pigments*, Vol. 64, pp. 63–71, 2005.

Scheer, H. (Ed). "*Chlorophylls*" *CRC* Press: BocaRa ton, FL.

Schramm, L.E.S., and B.M. Hoffman., *Inorg. Chem*., Vol. 19, pp. 383, 1980.

Seotsanya-mokhosi, I., N. Kuznetsova, and J. T. Nyokong, *Journal of Photochemistry and Photobiology* A: Chemistry, Vol. 140, pp. 215–222, 2001.

Sesalan, Ş.B., and A. Gül, *Monatshefte für Chemie*, Vol. 131, pp. 1191, 2000.

Sibert, J.W., T.F. Baumann, D.J. Williams, A.J.P. White, A.G.M. Barrett, and B.M. Hoffman, J. Am .*Chem. Soc*., Vol. 118, pp. 10487, 1996.

Snow, A. W., W. R. Barger, and M. Klusty, *Langmuir*, Vol. 2, pp. 513, 1986.

Spasojevic, I., and I. Batinic-Haberle, *Inorg. Chim*. Acta., Vol. 317, pp. 230, 2001.

Stihler, P., B. Hauschel, and M. Hanack, *Chem. Ber*., Vol. 130, pp. 801–806, 1997.

Stuzhin, P. A., C. Ercolani, in "*The Porphyrin Handbook*" (Eds K. M. Kadish, K. M. Smith, R. Guilard), Academic Press: NewYork, NY, Vol. 15, pp. 263, 2003.

Stuzhin, P.A., and O.G. Khelevina, *Koord. Khim*., Vol. 24, pp. 782, 1998.

Stuzhin, P.A., E.M. Bauer, and C. Ercolani, *Inorg. Chem*., Vol. 7, pp. 1533, 1998.

Stuzhin, P.A., O.G. Khelevina, and B.D. Berezin, "*Phthalocyanines: Properties and Applications*", C.C. Leznoff, and A.B.P. Lever N. (Eds.), New York: VCH, Vol. 4, 1996.

Sun, J., Y. Sun, K. Deng, H. Hou, and D. Wang, *Chem. Lett.*, Vol. 36, pp. 586, 2007.

Svetkina, E. Yu., T. V. Filippova, E.A. Blyumberg, and V. N. Kopranenkov, *Kinet. Katal*., Vol. 25, pp. 1101, 1984.

Tabata, K., K. Fukushima, K. Oda, and I. Okura, *J. Porphyrins Phthalocyanines*, Vol. 4, pp. 278–284, 2000.

Thompson, J. A., K. Murata, D. C. Miller, J. L. Stanton, W. E. Broderick, and B. M. Hoffman, J. A. Ibers, *Inorg. Chem*., Vol. 32, pp. 3546–3553, 1993.

Uchida, H., P. Reddy, S. Nakamura, and T. Toru, *J.Org. Chem*., Vol. 68, pp. 8736, 2003.

Uslu, R.Z., and A. Gül, C. R. Acad. Sci. Paris, Ser. II C : Chim., Vol. 3, pp. 643, 2000.

Vagin S., G. Y. Yang, M. K. Y. Lee, and M. Hanack, *Optics Commun*., Vol. 228, pp. 119-125, 2003.

Vagin, S., M. Barthel, D. Dini, and M. Hanack, *Inorg. Chem*., Vol. 42, pp. 2683, 2003.

van Nostrum, C.F, and R.J.M Nolte, *Chem. Commun*., pp. 2385, 1996.

van Nostrum, C.F., F.B.G. Benneker, H. Brussaard, H. Kooijman, N. Veldman, A.L. Spek, J. Schoonman, M.C. Feiters, and R.J.M. Nolte, *Inorg. Chem*., Vol. 35, pp. 959, 1996.

Villanueva, A., L. Caggiari, G. Jori, and C. Milanesi, J. *Photochem. "Photobiol*.", B: Biol., Vol. 23, pp. 49, 1994.

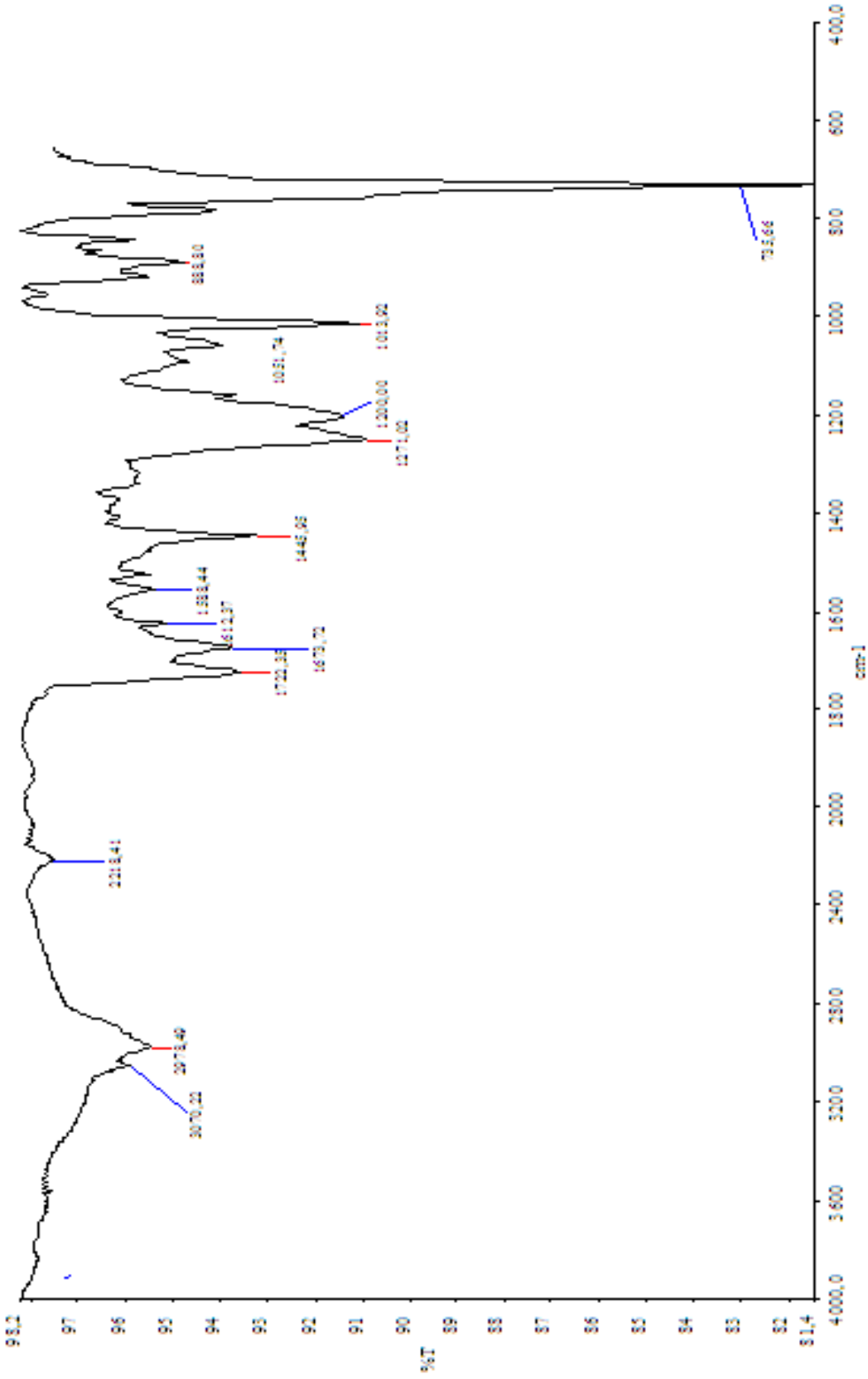
Weiss, C., H. Kobayashi, and M.J. Gouterman, *Mol. Spectrosc*., Vol. 16, pp. 415, 1965.

Wolf, W., E. Degener, and S. Petersen., *Angew. Chem*., Vol. 72, pp. 963, 1960.

Yenilmez, H.Y., İ. Özçeşmeci, A.İ., Okur and A. Gül, "*Polyhedron*", Vol. 23, pp. 787, 2004.

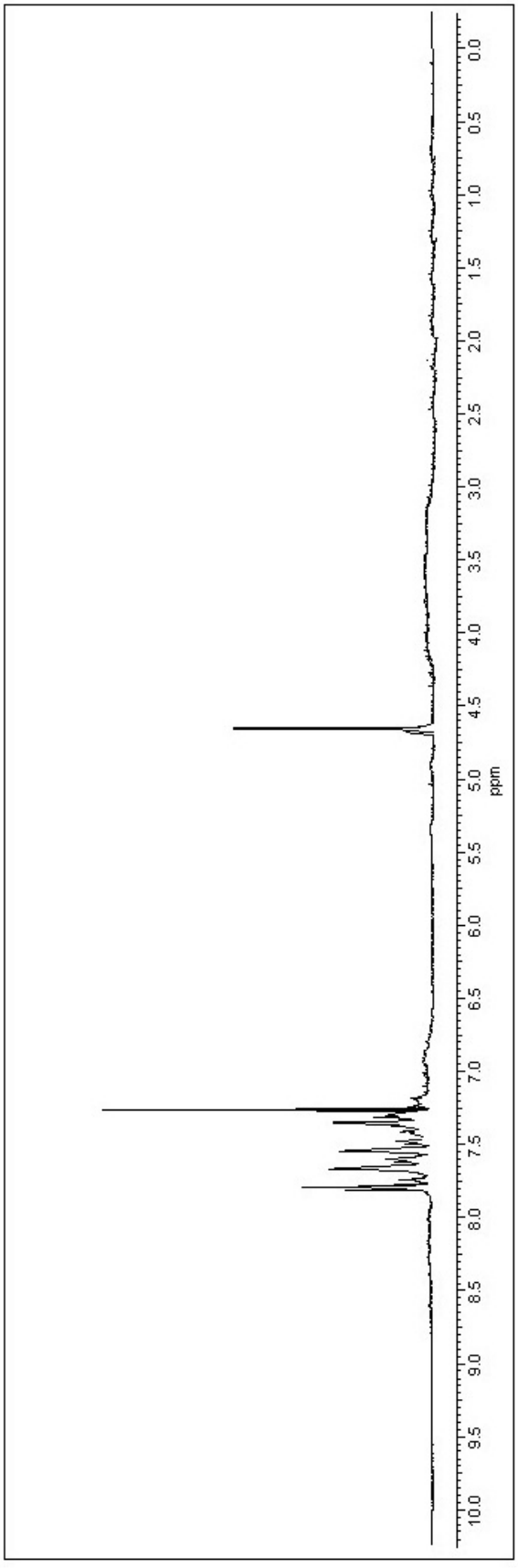
Zhao, M., Ph.D. Thesis in Northwestern University, 2004.

APPENDIX A



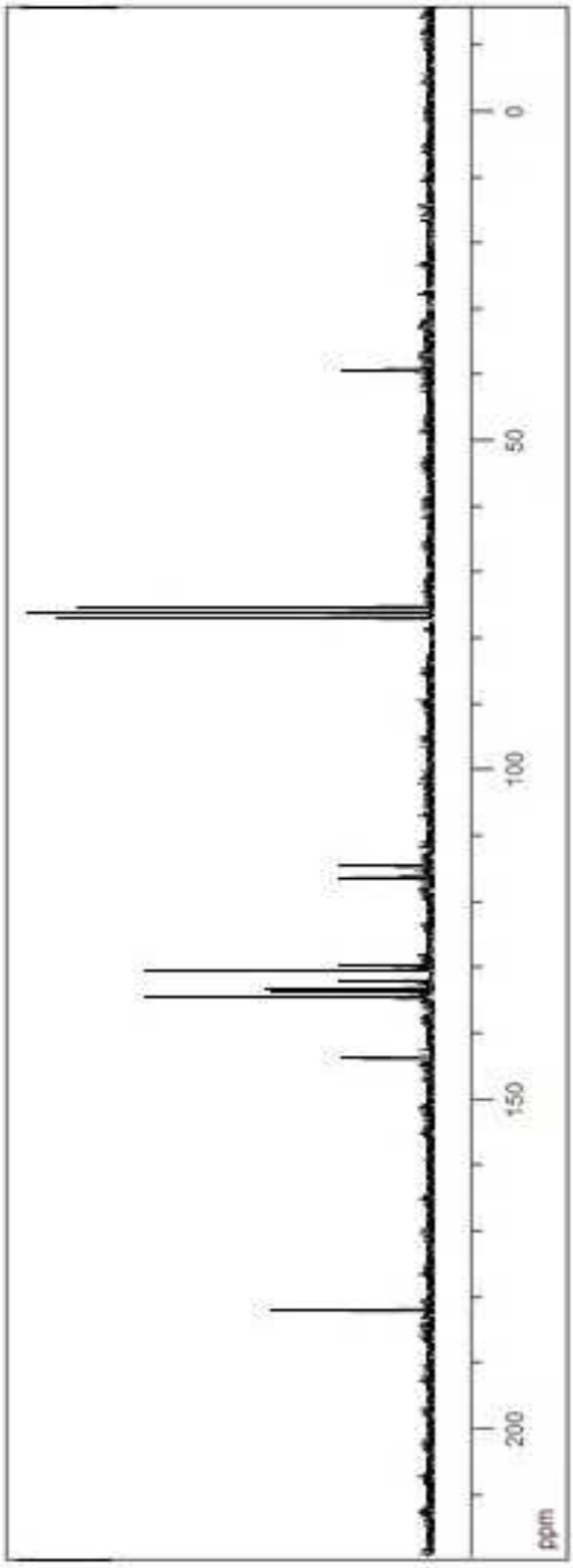
FT-IR Spectrum of 2,3-bis (2-anthraquinonylmethylthio) maleonitrile (**2**)

APPENDIX B



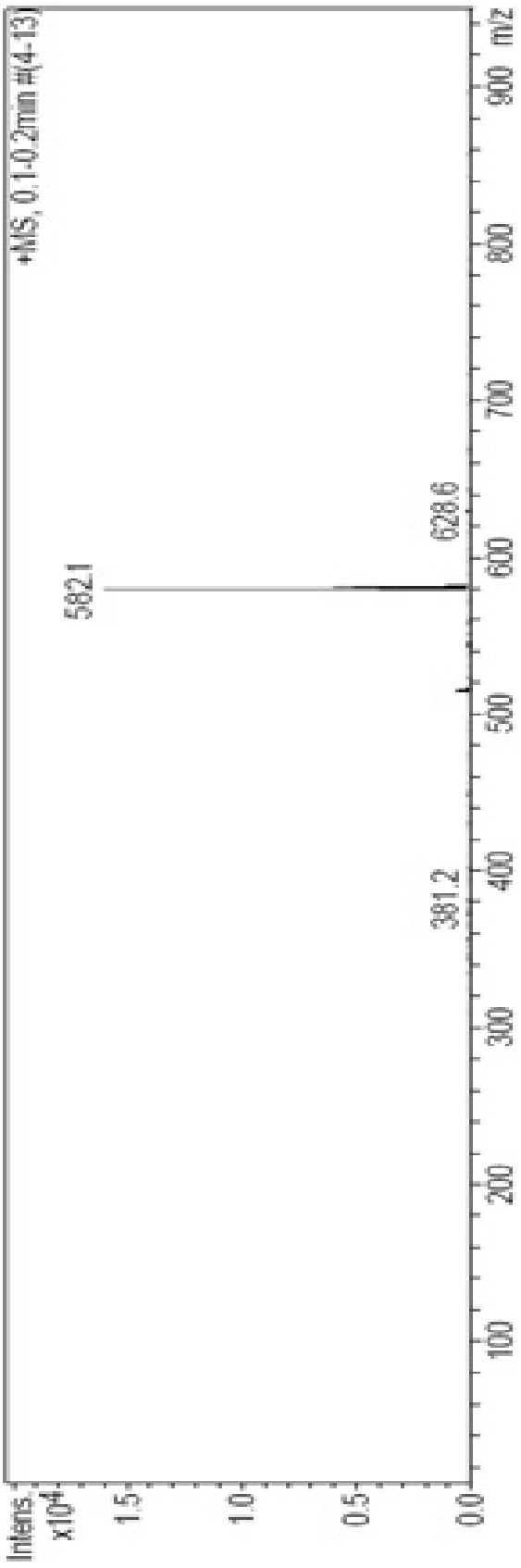
^{1}H NMR Spectrum of 2,3-bis (2-anthraquinonylmethylthio) maleonitrile (**2**)

APPENDIX C



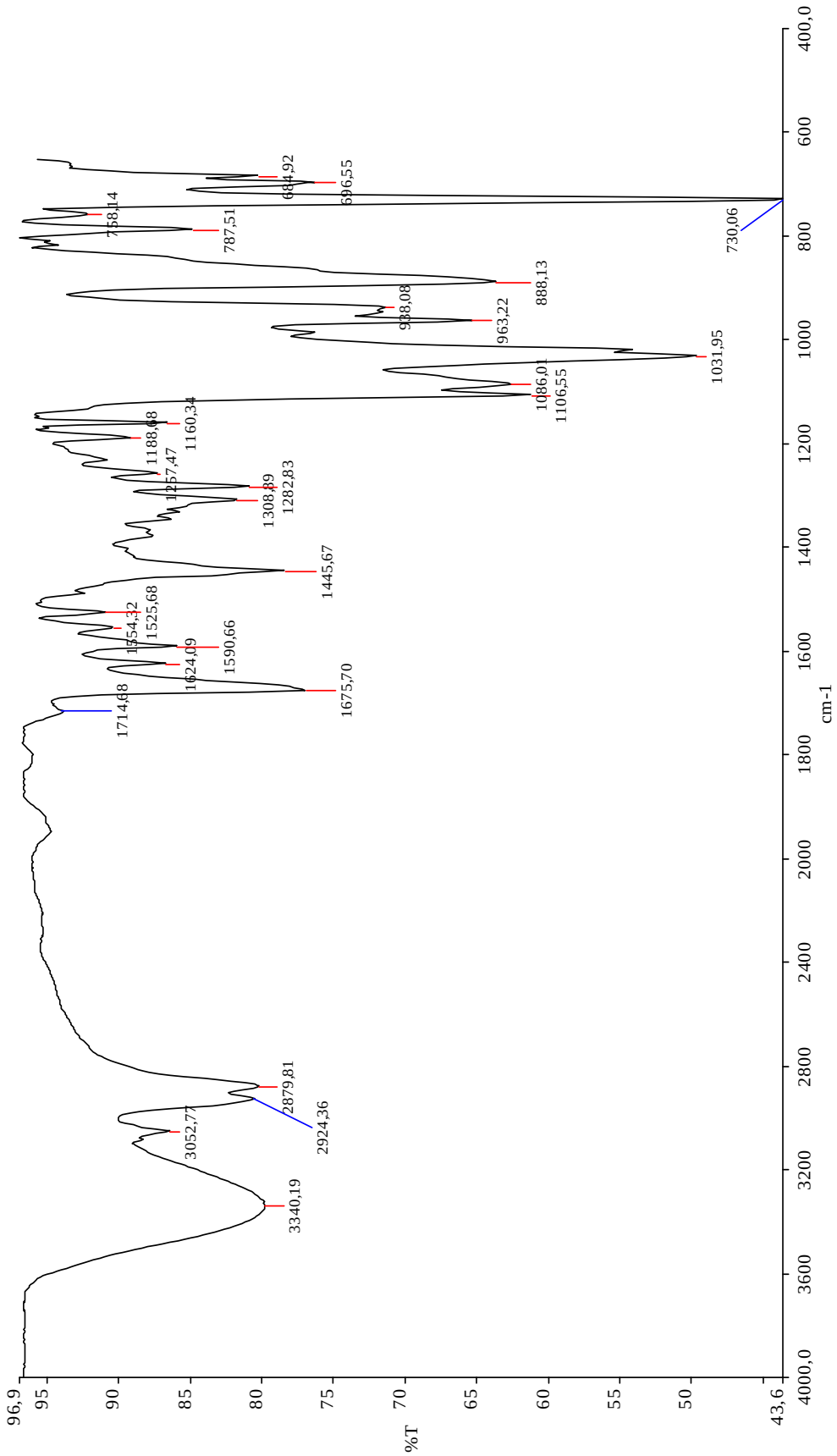
^{13}C NMR Spectrum of 2,3-bis(2-anthraquinonylmethylthio) maleonitrile (**2**)

APPENDIX D



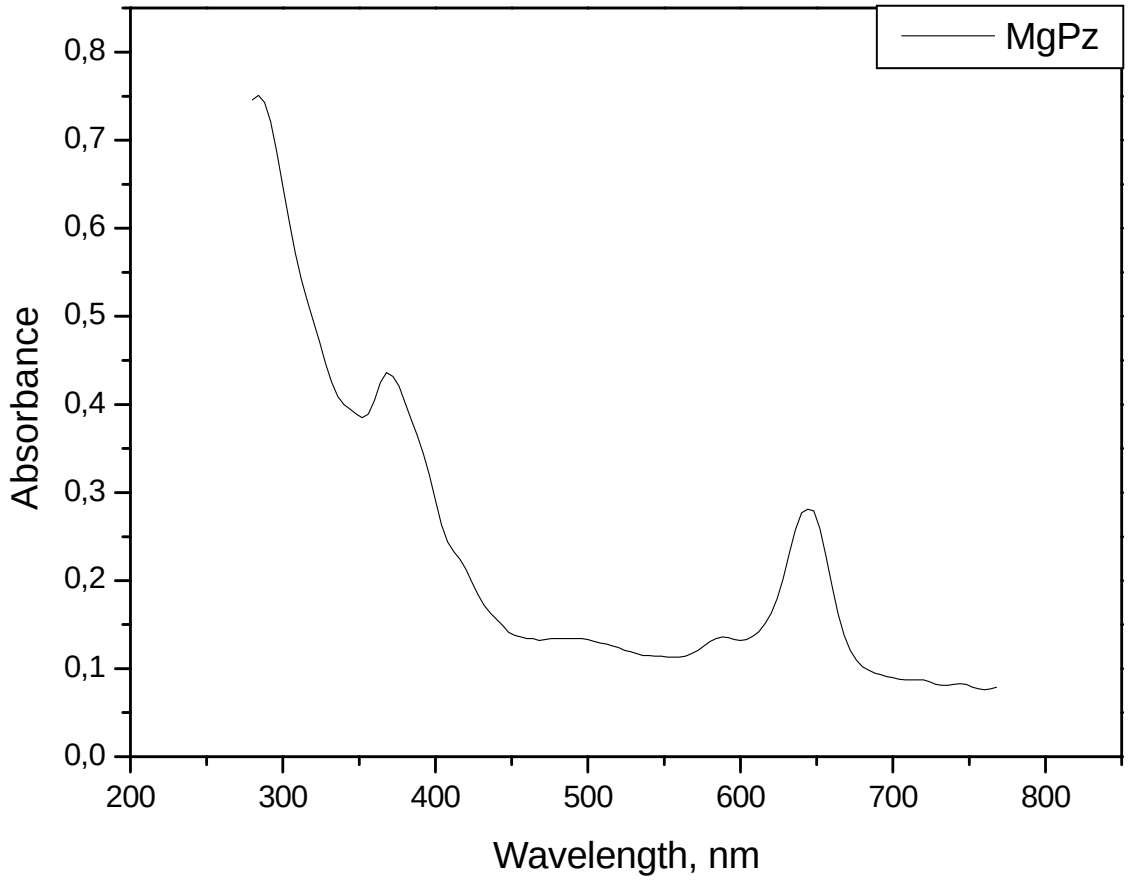
Mass Spectrum of 2,3-bis (2-anthraquinonylmethylthio) maleonitrile (**2**)

APPENDIX E



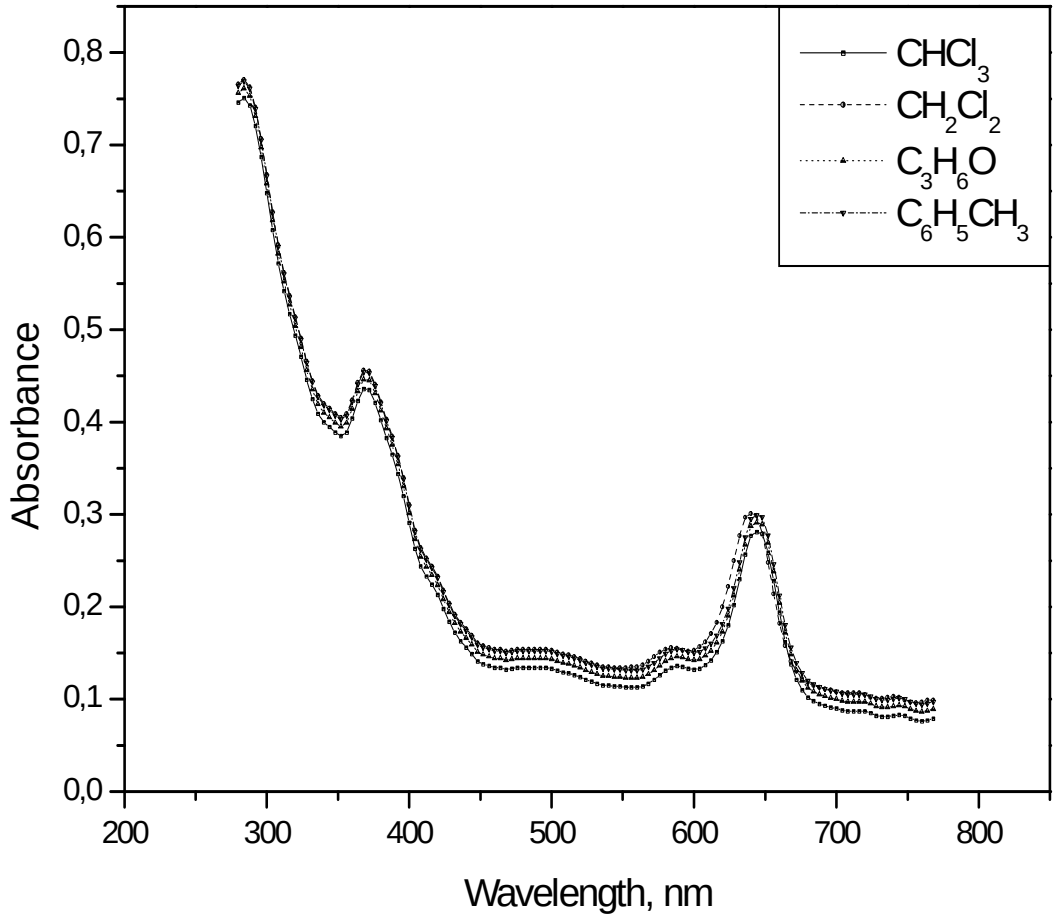
FT-IR Spectrum of [2,3,7,8,12,13,17,18-octakis(2-anthraquinonylmethylthio) porphyrazinato] Mg(II) (**3a**)

APPENDIX F



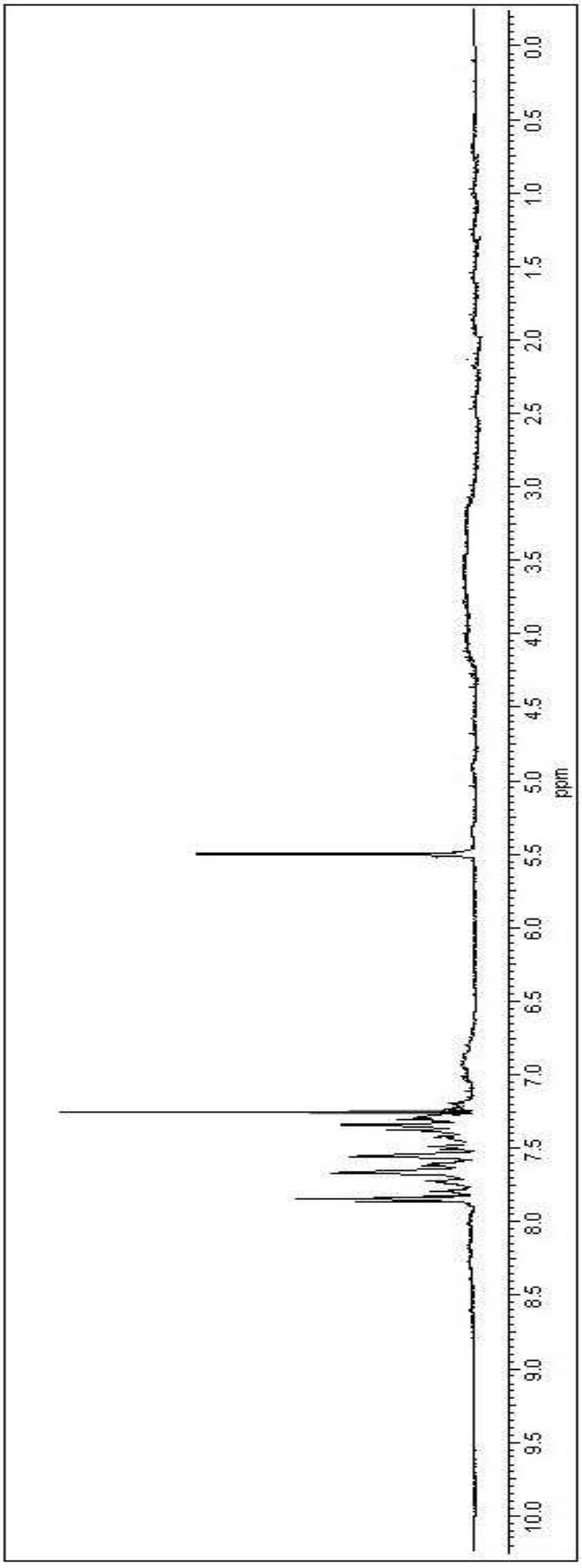
UV-Vis Spectrum of MgPz (**3a**) in $CHCl_3$

APPENDIX G



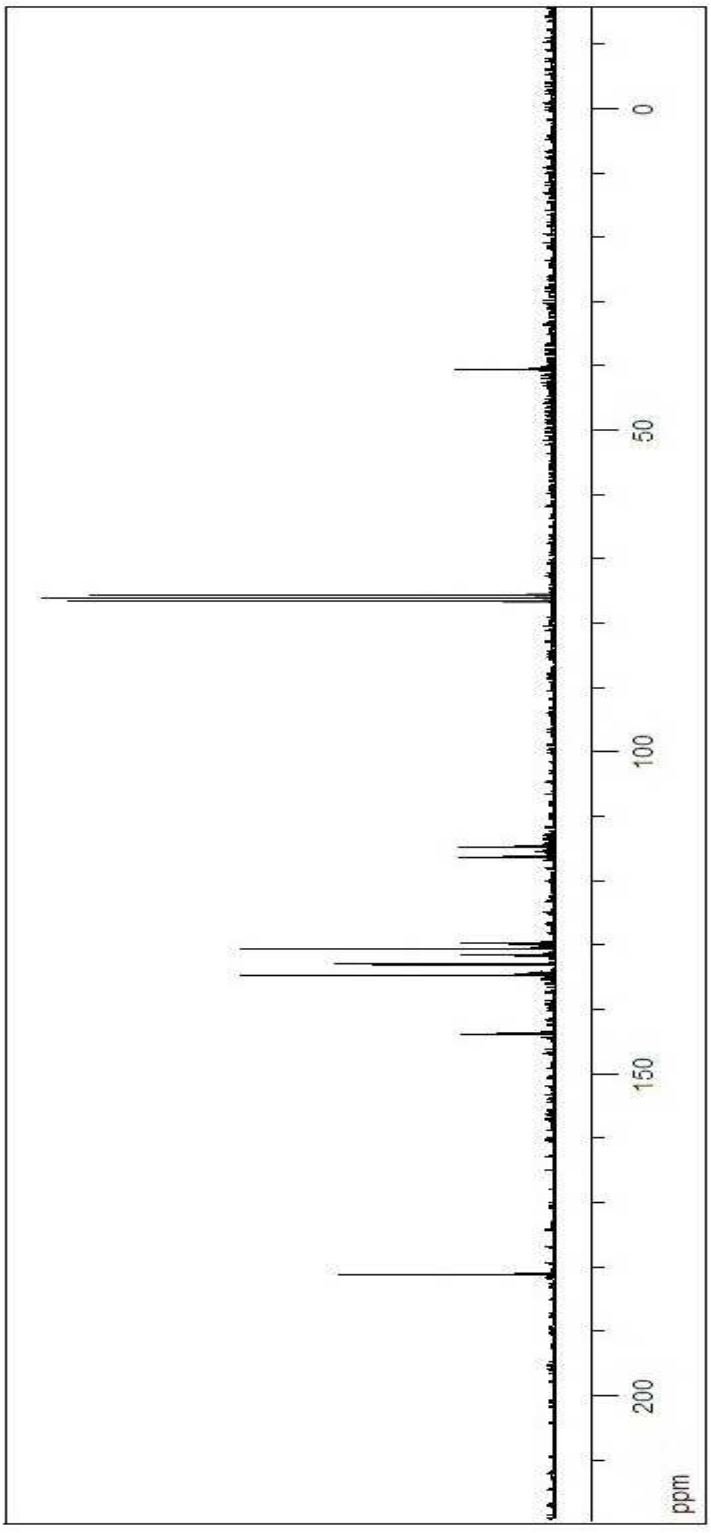
UV-Vis Spectra of MgPz (**3a)** in Various Solvents

APPENDIX H



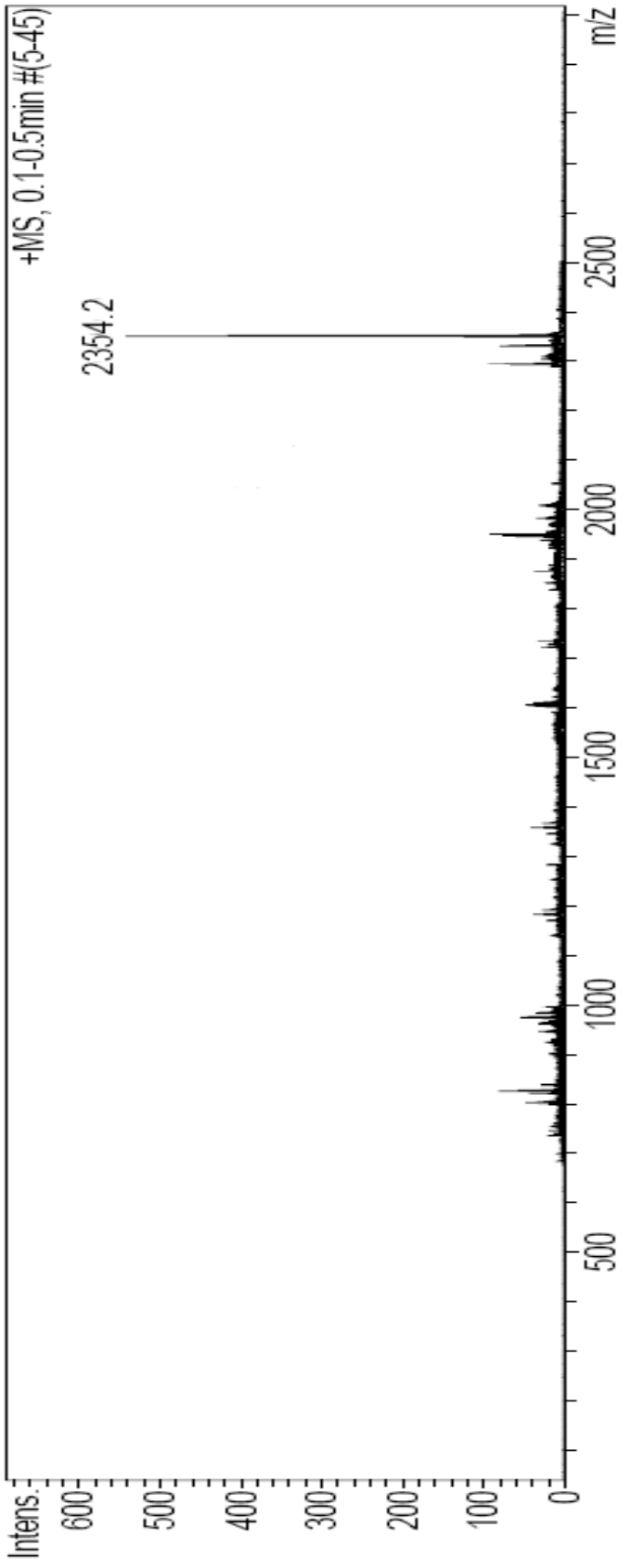
^{1}H NMR Spectrum of MgPz (**3a**)

APPENDIX I



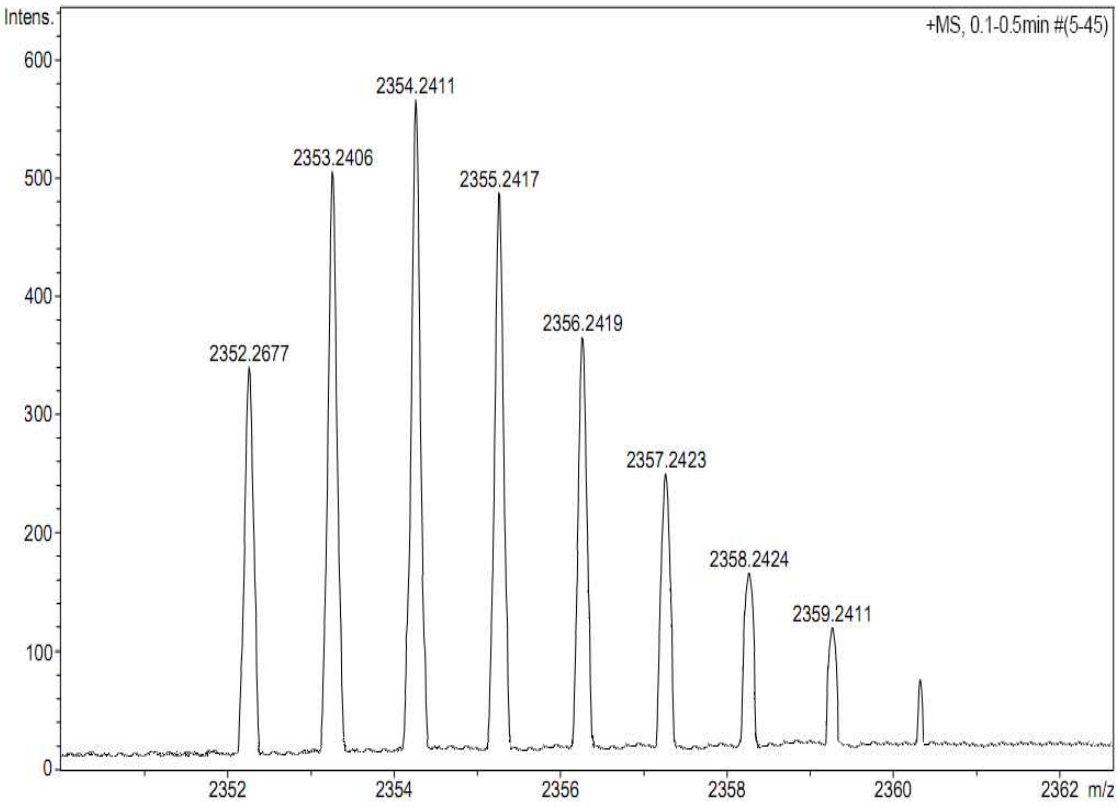
^{13}C NMR Spectrum of MgPz (**3a**)

APPENDIX J



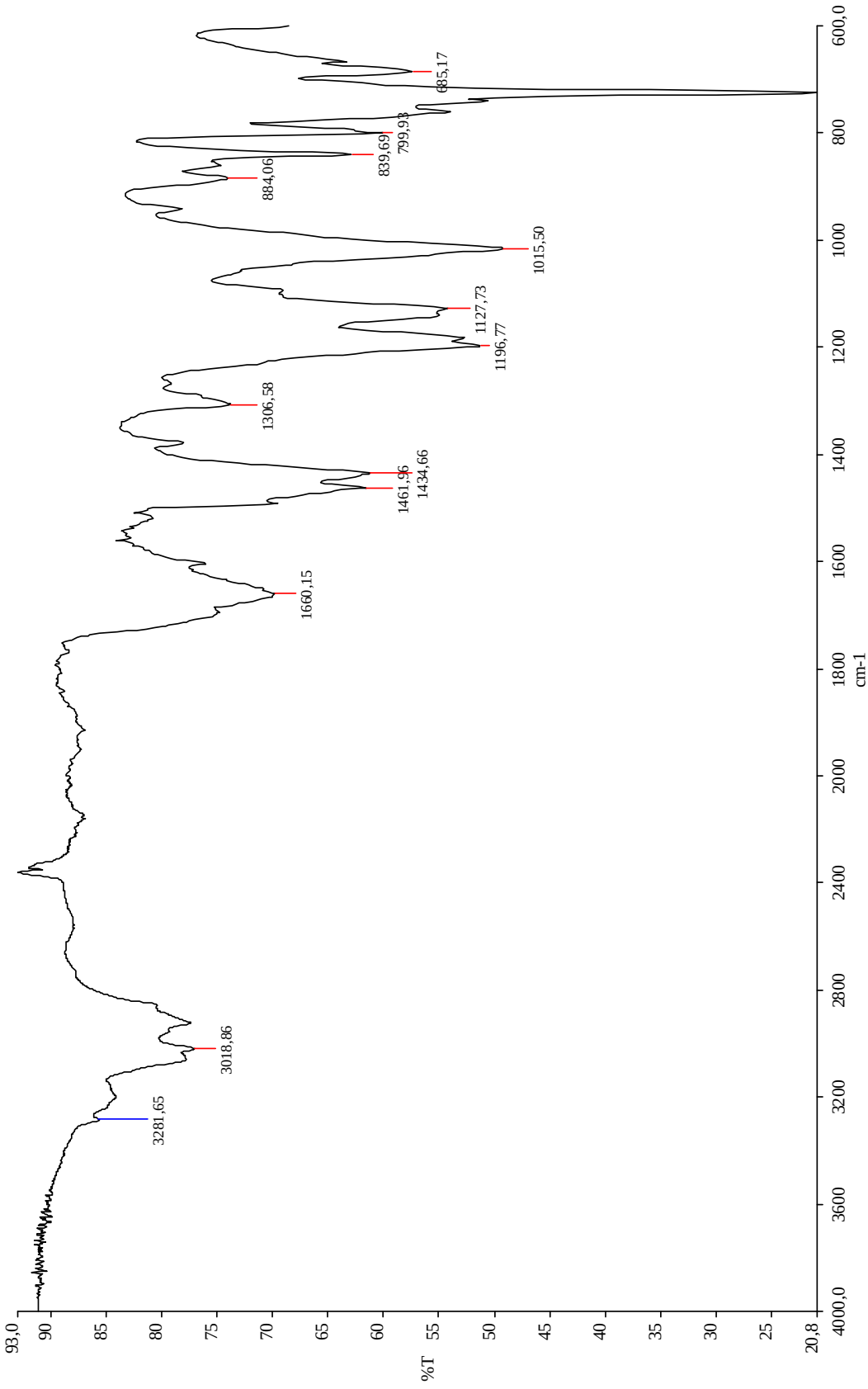
Mass Spectrum of MgPz (**3a**)

APPENDIX K



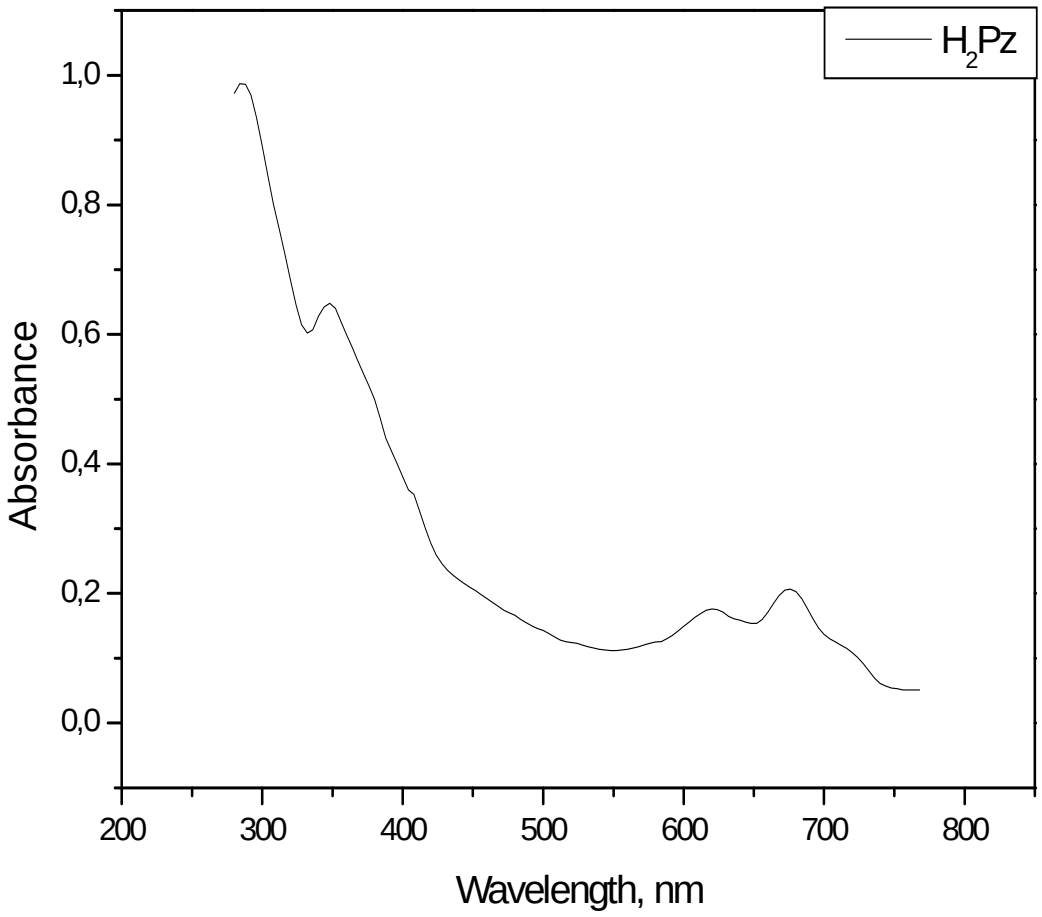
Mass Spectrum of MgPz (**3a**)

APPENDIX L



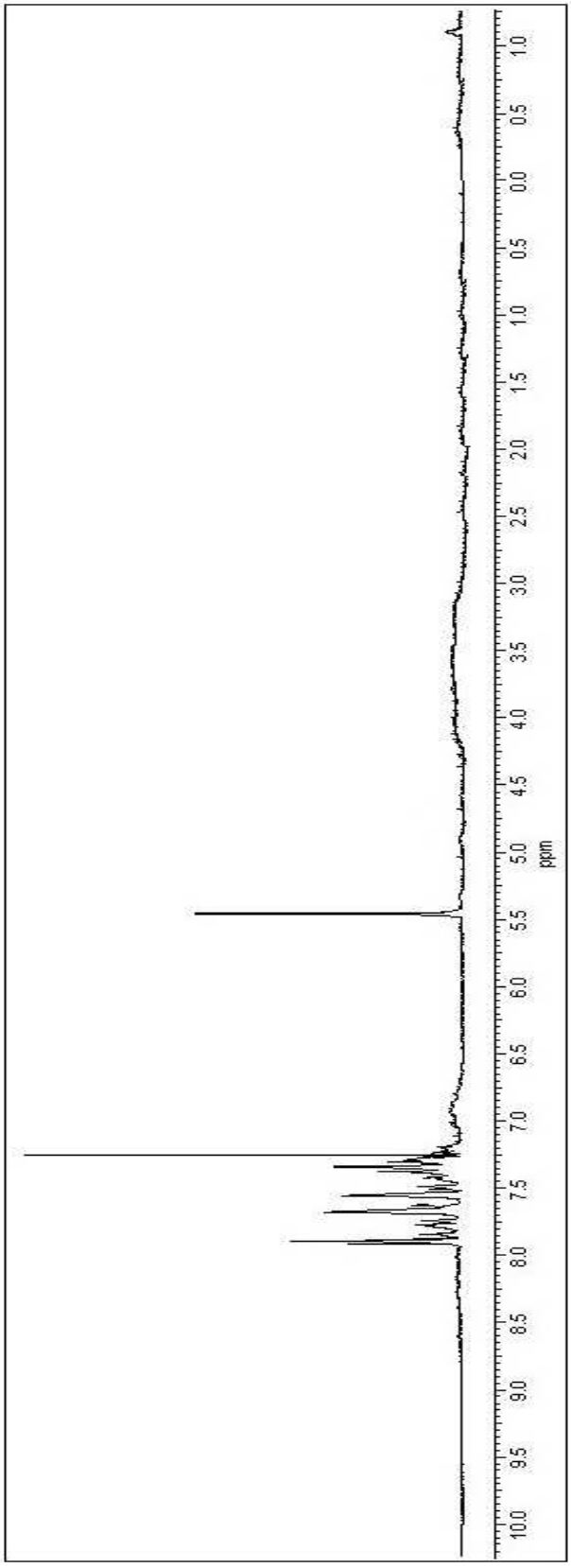
FT-IR Spectrum of H_2Pz (**3b**)

APPENDIX M



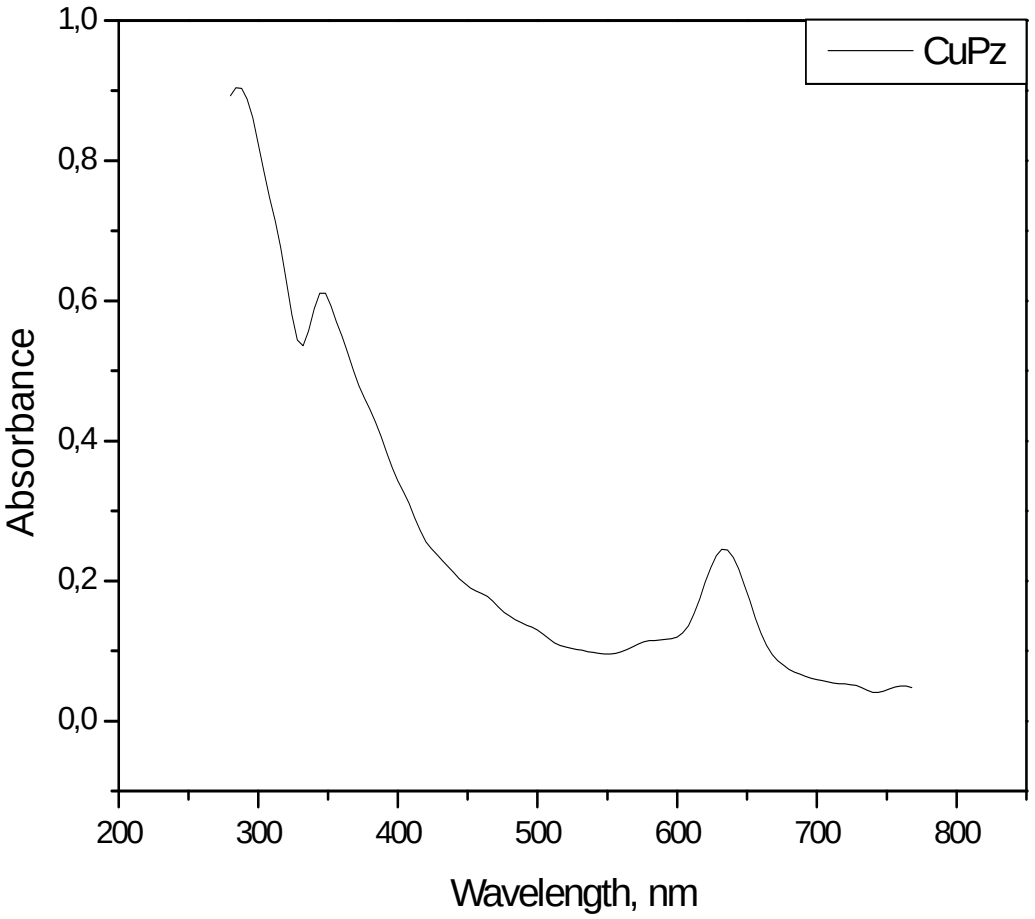
UV-Vis Spectrum of H_2Pz (**3b**) in $CHCl_3$

APPENDIX N



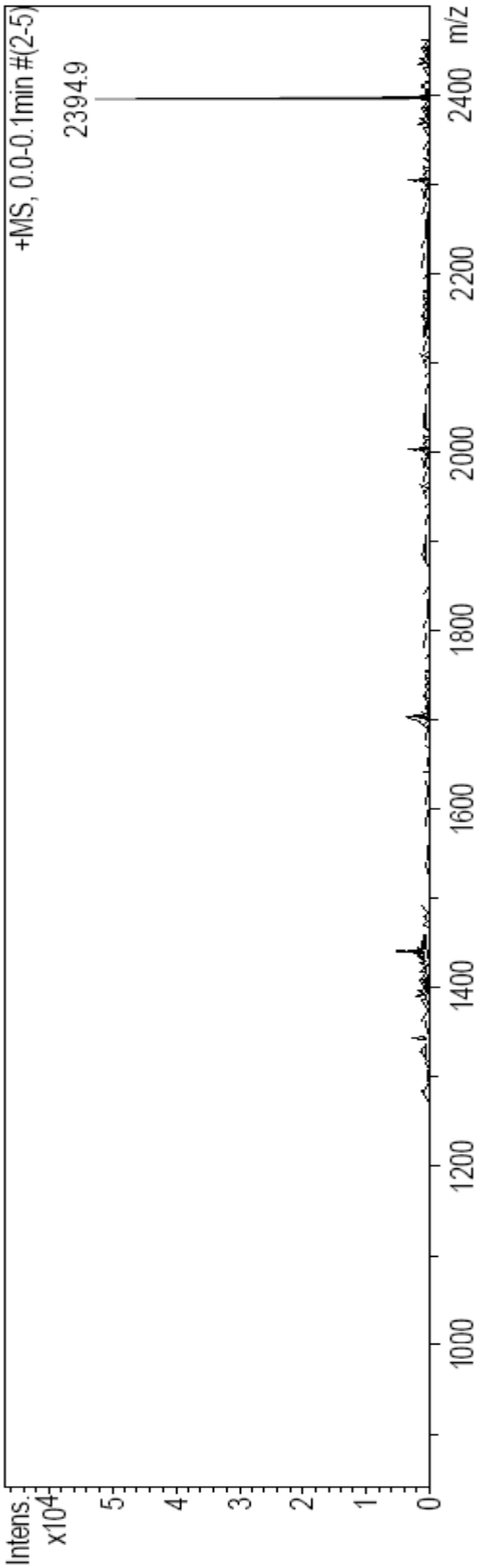
^{1}H NMR Spectrum of H_2Pz (**3b**)

APPENDIX O



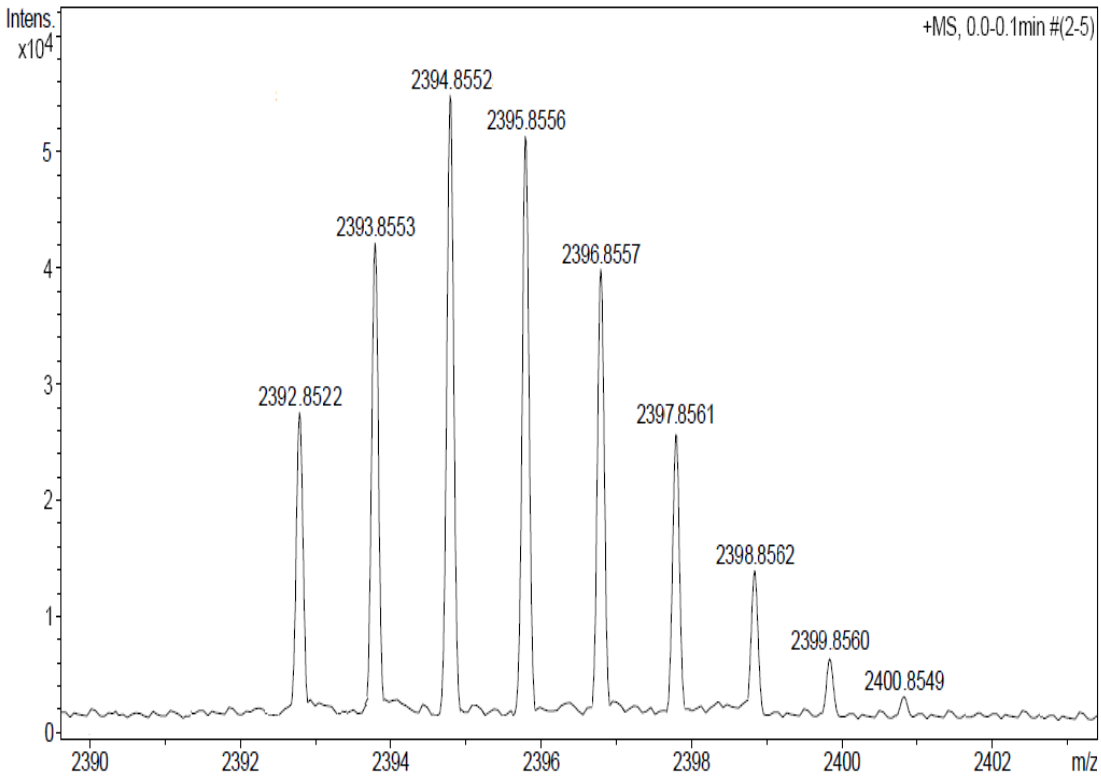
UV-Vis Spectrum of CuPz **(3c**) in $CHCl_3$

APPENDIX P



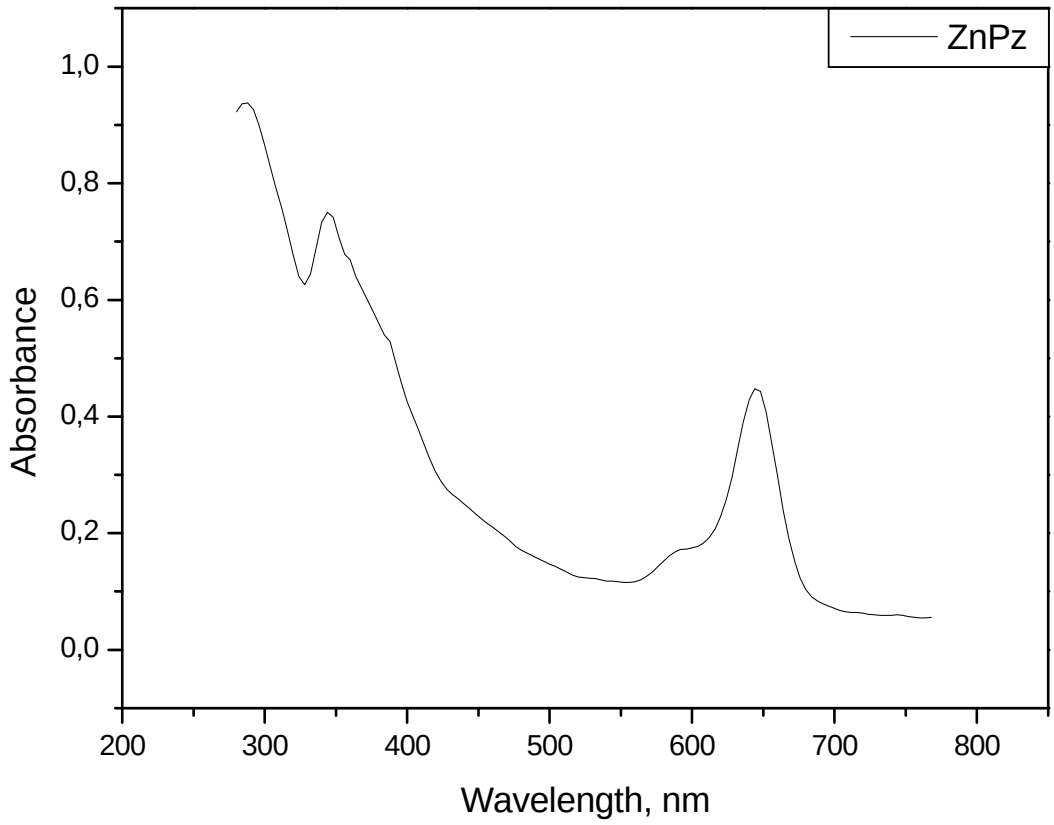
Mass Spectrum of CuPz (**3c**)

APPENDIX Q



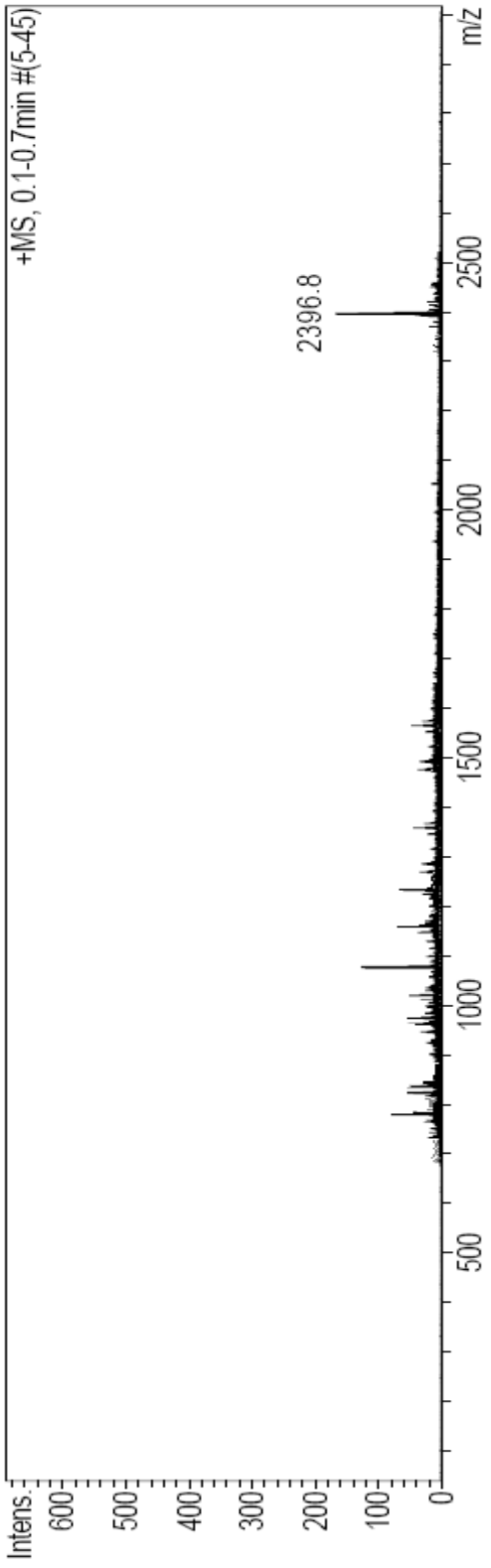
Mass Spectrum of CuPz (**3c**)

APPENDIX R



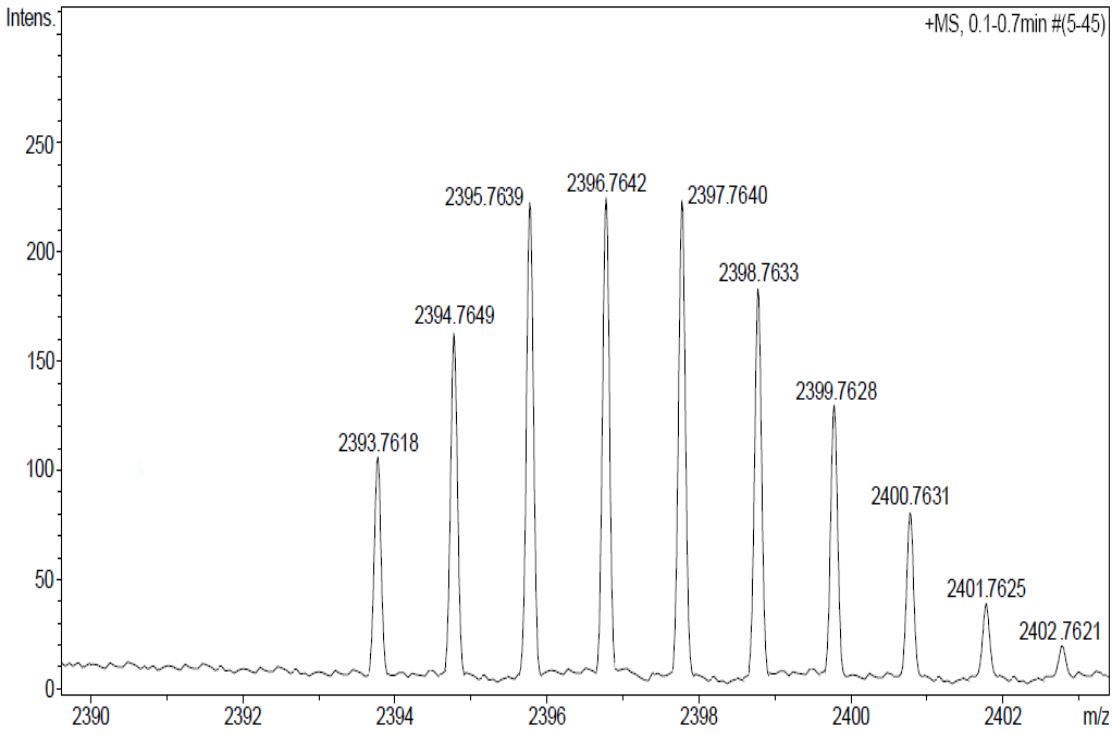
UV-Vis Spectrum of ZnPz (**3d**) in $CHCl_3$

APPENDIX S



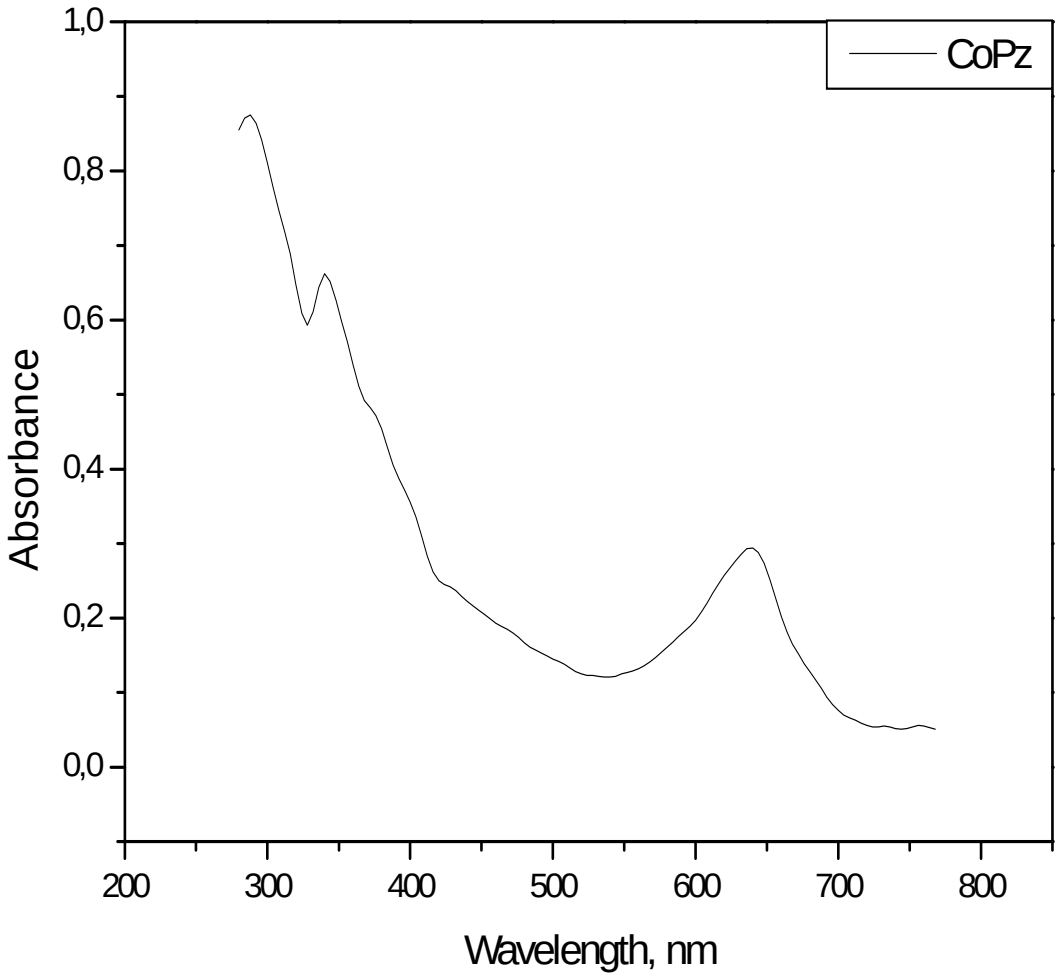
Mass Spectrum of ZnPz (**3d**)

APPENDIX T



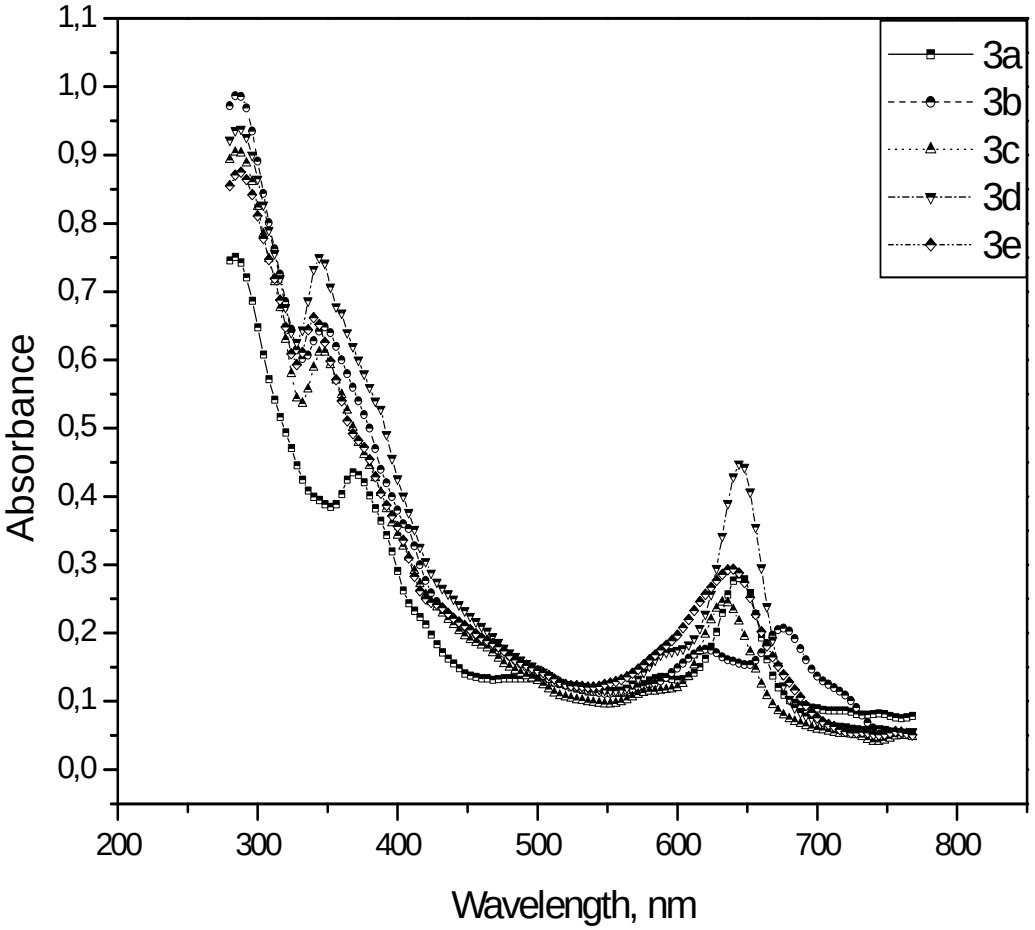
Mass Spectrum of ZnPz (**3d**)

APPENDIX U



UV-Vis Spectrum of CoPz (**3e**) in $CHCl_3$

APPENDIX V



UV-Vis Spectra of (**3a-3e**) in $CHCl_3$